

Chemistry Projects — Special Section

# CHEMISTRY

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### Editorial:

You Must Play Science  
Inside Front Cover

50¢

SEPTEMBER  
1957

★ A SCIENCE SERVICE PUBLICATION ★

# You Must Play Science

➤ YOUNG SCIENTISTS in high schools are learning by doing. That is about the only effective way they can learn in science.

Listening to teachers talk, watching movies and TV, viewing expertly done demonstrations, and reading about experiments in books — these are "spectator science." Unless minds are disturbed and hands are dirtied, science does not really take.

Young scientists to train for our civilization's future must get down out of the bleachers and out upon the playing field. They must "play science."

This is the objective of the great national science youth program that is sweeping America. This is the reason for October being designated as National Science Youth Month, a mechanism for getting the new school year science activities under way.

For nearly two decades science clubs and science fairs, fostered by Science Service, have urged the do-it-yourself method of science teaching and hobby activity.

Projects are integral and important parts of the National Science Fair and Science Talent Search methods. As examples of top projects submitted in the Science Talent Search for the Westinghouse Scholarships, CHEMISTRY in this issue publishes eight chemical project reports.

After an extensive survey just completed at the instance of the American Association for the Advancement of Science, Drs. Margaret Mead and Rhoda Metraux, reaffirm the importance of student participation in science teaching, suggesting:

"Encourage more participation and less passive watching in the classroom, less repeating of experiments the answers to which are known. Give more chance to the students to feel they are doing it themselves."

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## Newest Element Christened Nobelium

► THE WORLD'S newest element, atomic number 102, has been christened nobelium, with No as its chemical symbol.

This designation was made official by the Commission on Nomenclature for Inorganic Chemistry of the International Union of Pure and Applied Chemistry at its July, 1957, Paris meeting.

Two elements were given new symbols. Einsteinium, a man-made element named after the late Albert Einstein, atomic number 99, will henceforth have Es as its symbol. Argon, a noble gas of atomic number 18, will have Ar as its symbol which has been used by other countries except the United States until now. The U. S. has used A until now.

Dr. Alexander Silverman, professor emeritus, University of Pittsburgh, and chairman of the commission on

nomenclature, said that in the future new elements will have a symbol of two letters, consisting either of the first two letters of the name, or the first letter in both the first and second syllables.

### Had Been Predicted

The heaviest man-made element, number 102, was created by an international team of scientists from Argonne National Laboratory, the British Atomic Energy Research Establishment at Harwell and Nobel Institute for Physics, Stockholm.

Only about 50 atoms, a completely unweighable amount, have been made.

The discovery of element 102 was predicted by Dr. Glenn T. Seaborg, University of California Nobel Prize-winning chemist, during the April, 1957, American Chemical Society

meeting in Miami, Fla. (CHEMISTRY, April, 1957.)

At that time Dr. Seaborg said he believed the next element would be discovered one atom at a time. He said techniques for the determination of atoms had been perfected to the point that individual atoms could be detected.

Dr. Seaborg, who is professor of chemistry and associate director of the University of California's Radiation Laboratory, had a part in the discovery of the preceding eight elements to be found and received the Nobel Prize in 1951 for his nuclear research.

The new element was found by bombarding curium, which is also a synthetic element, with carbon ions accelerated to great speeds in the Nobel Institute's cyclotron, or atom-smasher.

The Institute where the work was performed is named in honor of the Swedish chemist, the late Alfred Nobel, who established the Nobel Prizes awarded annually for outstanding contributions in the arts and sciences.

The form of nobelium made by the international team is reported to have an atomic mass number of 253. It is very unstable, having a half life of about ten minutes. When the nobelium decays, one way by which it was identified, it emits alpha particles, which are the nuclei of helium atoms.

It was also identified by its chemical behavior in a standardized zeo-carb resin column.

#### Fourth Recent Discovery

Nobelium is the fourth element scientists have discovered in the past three years. Elements 99 and 100,

einsteinium and fermium, were found jointly by groups at Argonne and at the University of California Radiation Laboratory when they examined the nuclear debris from the first hydrogen bomb explosion in November, 1952. First reports of the discoveries appeared in 1954.

Element 101, mendelevium, was first made in 1955, by Dr. Seaborg and his associates at the California Laboratory. Only 17 atoms, an almost unimaginably small amount, were synthesized. At the Paris meeting of the IUPAC the symbol for mendelevium was designated as Md. This replaced Mv which had come into common use. Some alphabets do not contain the letter "V."

The scientists cooperating in discovery of element 102 were Paul R. Fields and Arnold M. Friedman of Argonne National Laboratory, John Milsted and Alan Beadle of Harwell, and Hugo Atterling, Wilhelm Forsling, Lennart Holm and Bjorn Astrom of the Nobel Institute for Physics.

The United States, through the Argonne National Laboratory, provided the very rare isotope curium 244, used in the experiments. The curium was shipped to Harwell, where it was prepared for the cyclotron bombardment. Harwell also provided the rare isotope carbon 13 that was used as the bombarding particle. The Nobel Institute provided the cyclotron, selected because it could furnish the intense speed for high-energy carbon 13 ions necessary for the experiments.

Prior to making element 102, Mr. Fields and his associates had theorized that the best chance of building



it would come from bombarding the heaviest element with the lightest possible particle. Curium is the heaviest element available in sufficient quantities for testing purposes and carbon ions are the lightest particles

that would create element 102.

*For a free 10 by 15 inch periodic table, showing the latest changes, send a stamped, self-addressed envelope to CHEMISTRY, 1719 N St., N.W., Washington 6, D.C., and request the periodic table.*

### Chemistry Library

#### Powerful New Chemical Could Revolutionize Agriculture

## Jack's Beanstalk Comes True

by HOWARD SIMONS

► A CHEMICAL that causes plants to develop like Jack's fabled beanstalk might very well re-shape the world's agriculture. It is called gibberellic acid (the beginning of the word is pronounced like the beginning of the word gibberish) and it promises to become a household and farmhold word.

The exact potential of the chemical is not as yet well known. In some cases, the scientists' studies of what gibberellic acid can do have far surpassed the scientists' dreams. In other cases, the scientists' dreams for gibberellic acid have far surpassed its capabilities.

Nevertheless, this chemical that causes plants to grow to two or three times their normal height, has also caused research on it to grow as rapidly and chemical manufacturers to market the drug at superspeed. Gibberellic acid has so far proven to be not only a plant growth promoter, but a research and industry promoter too.

What exactly can gibberellic acid do?

#### Not a Cure-all

Most scientists agree with Dr. Paul C. Marth of the U. S. Department of Agriculture's plant industry station at Beltsville, Md., who says right off that the chemical is not a cure-all. Dr. Marth points out that much more research will be needed before gibberellic acid can be used effectively by the nation's farmers. Even then, Dr. Marth cautions, the drug will have to be tailored for use, taking into consideration the crop, season, soil, climate and, above all, the intended goal.

But even with these restrictions, a score of research teams throughout the world are reporting fantastic results with the chemical and it looks like the revolutionary growth promoter will live up to its advance notices.

Generally, gibberellic acid has been credited with not only stimulating plant growth, but causing earlier flowering, faster germination, speedier seed maturation and tailored dormancy.

#### Examples

Specifically, here are a few examples of what gibberellic acid has

been found to do: increase the number of tobacco leaves; create stronger and longer cotton fibers; cause significant increases in both the fresh weight and dry matter in celery; cause earlier heading in broccoli; cause some tree seedlings to grow faster; and create giant poinsettias, geraniums, chrysanthemums and roses.

Some of the results have been direct, such as the stimulating of Kentucky bluegrass. This particular study, reported by Drs. Curt Leben of Eli Lilly and Company and Lela V. Barton, Boyce Thompson Institute for Plant Research, may mean green lawns in the winter — at least in the warmer climates. Bluegrass sprayed with the acid in October, its slow growth season, shot up with bright green leaves in four days.

Other results will mean a use of the chemical that can mean indirect benefit for the farmer. E. A. Helgeson and John G. Green of the North Dakota Agricultural Experiment Station report, for example, that gibberellic acid is a new weapon against wild oats.

The dormancy of the seeds of wild oats, they explain, has been a challenging hindrance to effective control of this annual weed. This dormancy, they report, affects the control of the weed in that seeds may germinate for several years following an initial infestation of cultivated soil. Now, however, gibberellic acid can break the dormancy of wild oat seeds. Using gibberellic acid, the North Dakota research team concludes, may mean effective control in the fall or early spring by stimulating the wild oat seeds to germinate.

### Changes Leaf Shape

A third example of gibberellic acid's work is a report on how the drug affects leaf shapes. Dr. Reed A. Gray, plant pathologist with Merck, Sharp & Dohme, reported that treated tomato leaves looked more like potato leaves; tobacco and African violet leaves became longer and more pointed at the tip; and pepper leaves became rough instead of smooth.

Whatever gibberellic acid does, it does it in a powerful way, for it only takes one or two parts per million to work its wonders.

As wonderful as the drug seems, however, scientists feel that they cannot stress enough the fact that much more work is needed. Overdosing, they point out, can cause undesirable effects in some plants such as death of the growing tips or fruit that is knocked off.

### Results Vary

In addition, different experiments on the same plant have yielded different results. Treated tomato plants in one study, for instance, grew taller and produced twice as many tomatoes as untreated plants. Another study showed "fruit development not affected" in tomato plants.

Drs. S. H. Wittwer and M. J. Bukovac of Michigan State University's department of horticulture sum up gibberellic acid research this way:

"While gibberellins produce many remarkable effects which can speed up production in a wide range of crops — and many more will be discovered — there is still much to be learned in their use. . . . Much laboratory, greenhouse and field testing is needed before the full power of the

gibberellins will be realized. By that time, the farmer will be able to buy ample quantities from commercial sources. Because of cost, present uses will probably be with high-value greenhouse, nursery and garden crops as a fruit setting agent and in seed production."

The history of this revolutionary growth promoter involves military secrecy and a strange international barter that has resulted in the drug's expanded research in this country.

The story begins in Japan in the late 1920's. A fungus called *Gibberella fujikuroi*, which causes the disease known to rice farmers as "the foolish disease," was wreaking havoc with the rice crops by elongating the stems of rice plants. In the 1930's, Japanese scientists, looking for a control of the disease, had isolated several crystalline compounds from fermentation broths. (A relative of this fungal disease in this country attacks corn and is known as corn root rot.)

The Japanese named the crystalline compounds, which had growth-promoting capabilities, Gibberellin A and Gibberellin B.

Much excited about their find and the fact that these compounds in only one part per million could cause abnormal plant development, the Japanese scientists published their reports in Japanese journals. At about this time, however, the Second World War broke out and Western scientists had only a vague knowledge of the Japanese discoveries. Some anguish was caused in this country with scientific rumors that the Japanese had a "secret weapon" for increasing food production.

At the same time, Army scientists

were experimenting with the fungal disease itself as a possible weapon to be used against Japanese rice crops. Nothing came of this study and at war's end the Army information on gibberellins was declassified.

But before American scientists became excited, British scientists had started an intensive study of the gibberellins and tried to make a synthetic compound. When American scientists became interested a few years ago, the drug was a rare item. The little available here, however, did enable Dr. Frank Stodola of the U. S. Department of Agriculture to study it and make the first American report on the microbiological synthesis of Gibberellins A and Z. Since then, American and British scientists have found a related compound with the same capabilities and it is now known as gibberellic acid.

The drug was still in short supply when Dr. P. W. Brian of Akers Research Laboratories, England, was visiting the USDA Beltsville Station in 1955. Interested in a drug called Amo-1618, a chemical that regulates plant growth, Dr. Brian offered Dr. John Mitchell of the Beltsville Station five grams of gibberellic acid for a like amount of Amo-1618.

Thus, a rather strange barter, in which British scientists received a chemical that stunts plants in exchange for a chemical that elongates plants, has resulted in a rapid research program in the United States that may end in a whole new world of agriculture.

*For reports of student projects with plant growth promoters, see pages 15, 19, and 28.*

## Organo-Metallic Compounds

► STUDIES OF organo-metallic compounds show promise of chemical developments that could have major implications in basic chemical research, plastics, silicones, and perhaps even in guided missile fuels.

Two Harvard University research workers, Drs. Dietmar Seyferth and F. G. A. Stone of Harvard's Mallinckrodt Chemical Laboratory, have begun a study of vinyl derivatives of metals, starting with a substitution of tin in vinyl compounds. They hope to expand their study to cover substitutions of other metals and metalloids to result in a group of new compounds which they say "may possibly display interesting physical and chemical properties."

Drs. Seyferth and Stone became interested in these new possibilities as a result of studies made of earlier organo-metallic compounds and studies of the vinyl chemistry of boron and silicon.

The new studies compare roughly with work which resulted in the development of silicones now widely used in materials ranging from low-temperature aircraft lubricants to eyeglasses cleaners and high temperature electrical insulation.

A vinyl compound is one containing a radical or group of two carbon and three hydrogen atoms per molecule, arranged in a characteristic or-

der ( $\text{CH}_2\text{:CH—}$ ) which can be added to or taken from molecules of other materials, greatly changing the physical and chemical behavior of the materials. A molecule of ordinary acetylene (used for welding) can add a molecule of hydrogen chloride (the gas that produces hydrochloric acid in water) to form vinyl chloride, an entirely different substance which is used as an intermediate in making many plastics.

The organic vinyl group appears in a variety of industrial and household products, including the vinyl plastics, Vinylite and Teflon. Inorganic silicon, in an oxide form, is the major constituent of ordinary sand. Because of chemical similarities, which are clearly demonstrated in Group IV of the periodic table of the elements, silicon has been substituted for carbon in producing silicones. A comparable substitution of the element boron has resulted in the so-called "exotic fuels" for guided missiles.

The first few of the possible new group of compounds prepared have been named vinyltin compounds. The new compounds developed thus far are solids at normal room temperature, most with melting points somewhat above room temperature and boiling points considerably above the boiling point of water at normal pressures.

# CHEMISTRY PROJECTS

from the

*Science*

*Talent*

*Search*



from physics, biology, medicine and other sciences.

The 40 finalists who were guests at the Science Talent Institute in Washington, D. C., March 7-11 included about a dozen high school seniors whose projects were in or closely related to chemistry. Eight of the project reports, some of them condensed in places, appear on the following pages. These project reports were received by Science Service during December 1956. Other student project reports will appear in future issues of CHEMISTRY.

The student or teacher interested in earlier reports in other fields will find many of them reprinted in the following *Science Service Chemistry Series* books, available at \$2.00 each, postpaid, from Science Service, 1719 N St., N.W., Washington 6, D.C.: SCIENTIFIC INSTRUMENTS YOU CAN MAKE, SCIENCE EXHIBITS.

➤ AMONG the thousands of participants in the 16th Annual Science Talent Search, conducted by Science Clubs of America for the Westinghouse Science Scholarships, there were many students who expressed their intentions to become chemists. Many of the submitted projects — the high school scientist's equivalent of thesis research — demonstrated an advanced knowledge not only of the fundamentals of chemistry, but also of highly specialized and little publicized branches of the science as well as an informed grasp of those more and more frequent areas where it is difficult to differentiate chemistry

## LIFT OUT SECTION

This 36-page section of Science Talent Search project reports may be taken from this issue of CHEMISTRY and filed separately with your STS material. Using a letter opener, spread the staples in the center of the magazine (between pages 24-25) and remove the lift out section.

# Cobalt Coordination Compounds

by WILLIS WILLARD BALDERREE, JR.  
Grants Pass High School, Grants Pass, Ore.

➤ THE ORIGINAL PROBLEM with which my research was concerned was to determine whether or not a compound containing a complex ion could be isolated. To resolve this problem, I conducted several experiments which yielded no evidence indicating that compounds containing complex ions could be isolated. I then turned to the literature of inorganic chemistry. I discovered that a multiplicity of such compounds could be prepared, of which those containing cobalt interested me the most. I therefore began work on the preparation of coordination compounds of cobalt, inasmuch as the solution to my original problem had been found.

## Preparation of Cobalt Complexes

To synthesize cobalt coordination compounds, I have formulated a general plan based upon my own experience and the information contained in various reference works. The first step is to prepare<sup>1</sup> the reactants. This involves weighing materials and making solutions of the desired concentration. Then the reactants are mixed, and any special conditions on which the reaction depends must be provided. These conditions are quite varied.

Sometimes the reaction mixture must be kept at a constant temperature. In some cases a stream of air must be passed through the solution for several hours. In the case of two compounds, it is necessary to pass nitric oxide through the solution for



➤ A COBALT COORDINATION COMPOUND containing complex ions is shown by Willis Willard Balderree during the 16th Science Talent Institute.

three hours.<sup>2</sup> In another instance six reacting solutions must be mixed within ten seconds.<sup>3</sup> Occasionally the reaction occurs without any special assistance. After the reaction is complete, the product is precipitated; collected on a filter; washed with such fluids as ice-cold water, ethanol, methanol, and ether; and dried. Of course, this plan is very general; a great deal of variation exists in each step among the individual syntheses.

## Individual Compounds

In the course of my work, I have followed the above procedure to synthesize over twenty coordination com-

pounds of cobalt. I should like to discuss some of these in terms of the interesting properties which they possess. Nitropentamminecobalt (III) chloride,  $[\text{Co}(\text{NH}_3)_5\text{NO}_2] \text{Cl}_2$ , and nitritepentamminecobalt (III) chloride,  $[\text{Co}(\text{NH}_3)_5\text{ONO}] \text{Cl}_2$ , are two compounds which, according to some sources, illustrate structural, or salt, isomerism.<sup>4</sup> However, other authorities do not hold this belief.<sup>5</sup> Potassium trioxalatecobaltate,  $\text{K}_3 [\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ , is interesting because of its photosensitive nature.<sup>6</sup> This is the only compound containing a complex anion<sup>7</sup> that I prepared. A compound containing tetra-valent cobalt, decammine- $\mu$ -peroxocobalt (III)-cobalt (IV) sulfate,  $[(\text{NH}_3)_5\text{Co}^{(\text{III})}(\text{O}_2)\text{Co}^{(\text{IV})}(\text{NH}_3)_5](\text{SO}_4)_2 \cdot \text{SO}_4\text{H} \cdot 3\text{H}_2\text{O}$ , exemplifies the stabilization of unusual valence states which occurs in coordination compounds.<sup>8</sup> This is a polynuclear complex, having two centers of coordination.<sup>9</sup> Trinitrotri-amine cobalt (III),  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ , is singular among the compounds prepared in being a non-electrolyte.<sup>10</sup> This property results from the coordination of three  $\text{NO}_2^-$  groups as well as three  $\text{NH}_3$  groups, thus satisfying not only the secondary, or coordinate, valence, but also the primary, or ionizable, valence. Tris (ethylenediamine) cobalt (III) chloride,  $[\text{Co}(\text{en})_3] \text{Cl}_3$ ,<sup>11</sup> illustrates the phenomenon of *chelation*,<sup>12</sup> or the occupation by one coordinated group of more than one position in the coordination sphere. The bidentate ethylenediamine groups span *cis* positions, of course.<sup>13</sup>

#### Series of Compounds

In addition to individual compounds and isomeric pairs, I have

prepared two series of coordination compounds. One is the acidopentamminecobalt (III) nitrates. Carbonate-pentamminecobalt (III) nitrate,  $[\text{Co}(\text{NH}_3)_5\text{CO}_3] \text{NO}_3$ , was the first member of this series that I prepared. Then, using this substance as a base, I substituted a nitrite, a nitrate, an acetate, and a fluoride for the carbonate. The rest of the complex ion remained unchanged, and the nitrate anion was retained; however, the number of nitrates increased to two in all cases because of the change of valence of the complex cation.

One compound resulting from the work on this series is of especial interest. This is fluoropentamminecobalt (III) fluoride nitrate,  $[\text{Co}(\text{NH}_3)_5\text{F}] \text{FNO}_3$ , a compound containing a double anion. The difference between the complex ion of the original member of this series, carbonatepentamminecobalt (III) nitrate,  $[\text{Co}(\text{NH}_3)_5\text{CO}_3] \text{NO}_3$ , and that of tetramminecobalt (III) chloride,  $[\text{Co}(\text{NH}_3)_4\text{CO}_3] \text{Cl}$ , is worthy of note. In the former compound the carbonate occupies only one position in the coordination sphere; but in the tetrammine salt, the carbonate is a bidentate chelate group. The other series is the hexamminecobalt (III) salts. In this series, unlike the acidopentamines, the complex cation,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , remained constant; and the anions changed.

Another compound which I have prepared is nitrosylpentamminecobalt (III) chloride,  $[\text{Co}^{(\text{III})}(\text{NH}_3)_5\text{NO}] \text{Cl}_2$ . This substance, together with nitrosylpentamminecobalt (II) chloride,  $[\text{Co}^{(\text{II})}(\text{NH}_3)_5\text{NO}] \text{Cl}_2$ , on which I am now working, constitute a pair of compounds which exemplify valence isomerism.<sup>14</sup> In the cobalt-

ous compound the NO group is neutral; but, in the formation of the cobaltic isomer, the cobalt atom transfers an electron to the NO group, yielding the cobalt trivalent and the NO group negative.<sup>15</sup>

In addition to these nitrosyl compounds, I plan to do further work with cobalt coordination compounds, such as aquepentamminecobalt (III) chloride,  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ , and bromopentamminecobalt (III) bromide,  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ . I expect to prepare at least one more member of the hexamine series, hexamminecobalt (III) oxalate,  $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3$ . Also, I plan to prepare iodopentamminecobalt (III) nitrate,  $[\text{Co}(\text{NH}_3)_5\text{I}](\text{NO}_3)_2$ , another member of the acidopentammine series.<sup>16</sup> As the topic of isomerism interests me, I wish to prepare some *cis-trans* isomers involving the coordination of ethylenediamine. Finally, I intend to do research on the problem of structural isomerism in nitropentamminecobalt (III) chloride,  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ , and nitritepentamminecobalt (III) chloride,  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ , which is mentioned earlier in this paper. At present I expect to direct my study of these compounds to the following objectives:

- (1) To test the comparative sensitivity of these compounds to acids.
- (2) To determine whether or not the red color of the nitrite compound is merely unreacted starting material. If my experiments indicate that this is true, I shall try to separate the unreacted material from the nitropentammine compound.

- (3) To conduct studies on the rate of transformation of the nitrite compound to the nitro isomer, and the effect of temperature on the rate of conversion.

## NOTES

1. This is the only use of the word "prepare" in a physical sense in this paper. In all other instances, "prepare" means "synthesize."

2. These are the nitrosylpentamminecobalt (II) chloride and nitrosylpentamminecobalt (III) chloride preparations, as described by Therald Moeller and Glendall L. King, "Nitrosylpentamminecobalt (II) Chloride (black) and Nitrosylpentamminecobalt (III) Chloride (pink)," in *Inorganic Syntheses*, John C. Bailar, Jr., ed., IV, 168-170.

3. This condition is required for the preparation of decammine- $\mu$ -peroxocobalt (III)-cobalt (IV) sulfate, as described by Georg Brauer, *Handbuch der Präparativen Anorganischen Chemie*, c. 1954, p. 1151.

4. H. J. Emeléus and J. S. Anderson, *Modern Aspects of Inorganic Chemistry*, pp. 109-110.

5. J. Lecemte and C. Duval: *Bull. sec. chim.* [5], 12, 678 (1945), reported in Therald Moeller, *Inorganic Chemistry*, p. 251.

6. John C. Bailar, Jr., and Eldon M. Jones, "Potassium Trioxalatecobaltate," in *Inorganic Syntheses*, Harold Simmons Booth, ed., I, 37.

7. *Ibid.*, p. 35.

8. Brauer, *loc. cit.*

9. *Ibid.*

10. William Edwards Henderson and W. Conrad Fernelius, *Inorganic Preparations*, p. 129.

11. *En* is an abbreviation for ethylenediamine,  $\text{C}_2\text{H}_4(\text{NH}_2)_2$ . This abbreviation is frequently used in writing



formulas of compounds in which ethylenediamine is coordinated.

12. J. B. Work, "Tris (Ethylenediamine) Cobalt (III) Chloride, in *Inorganic Syntheses*, W. C. Fernelius, ed., II, 221.

13. Bidentate groups can occupy only *cis* positions. See Therald Moeller, *Inorganic Chemistry*, p. 262.

14. Moeller and King, *op. cit.*, p. 170.

15. *Ibid.*

16. Two of the intermediate products of this synthesis have already been prepared. These are carbonatepentamminecobalt (III) iodide,  $[\text{Co}(\text{NH}_3)_5\text{CO}_3] \text{I}$ , and aquepentamminecobalt (III) iodide,  $[\text{Co}(\text{NH}_3)_5 \text{H}_2\text{O}] \text{I}_3$ .

## Effect of Electrical Discharge on Organic Compounds

by WARREN LOUIS BRAND

Phoenix Camelback High School, Phoenix, Ariz.

### Introduction

► THE EFFECT OF an electric discharge on organic compounds and the resulting reactions have interested the writer for two reasons: an inherent interest in organic chemistry and the fascination of an electric discharge. In an electric discharge it seemed that the heat energy, ionizing effect, and even actinic energy might produce interesting effects on organic compounds via the rupturing of bonds and subsequent free radical formation. The variety of reactions which free radicals undergo leaves possibilities for the formation of many products. Most free radical reactions are promoted by the use of thermal "cracking" which sometimes results in the partial decomposition of the compound undergoing the cracking. It seemed that the electric discharge, because of its added ionizing power, might disrupt organic bonds more easily than purely thermal methods.

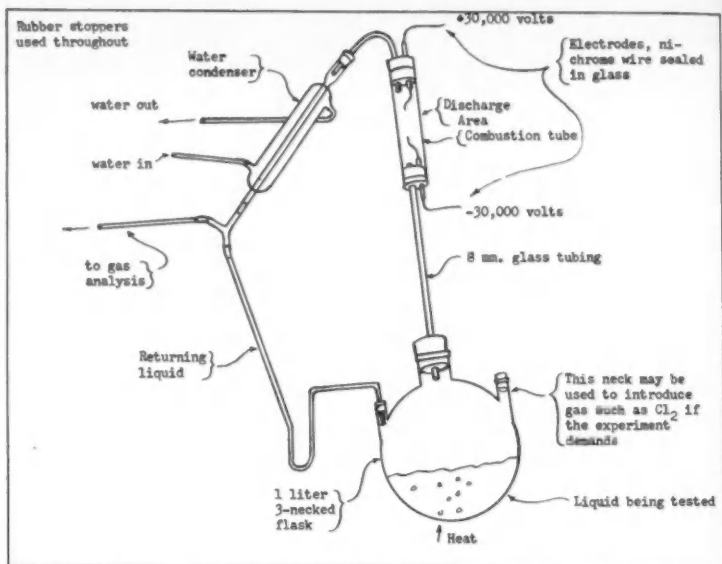
### Objectives

The object of the experiment was

to make a systematic survey of the effect of an electric discharge on organic compounds and, if possible, to correlate the observations with the compound's structure and its free radical mechanism. The project began with simple organic compounds and went on to more complex organic compounds.

### General Procedure

Research was begun approximately one and a half years ago on simple gaseous hydrocarbons. These were subjected to electric discharges, and products were analyzed as far as possible with the available equipment. Alcohols, acids, halogen substituted hydrocarbons, and some organic reactions were studied under the influence of the discharge. In every case suitable controls, which were the exact replica of the experiments without the discharge, were used. Many of the experiments resulted in no detectable reactions to the discharge, while others proved more interesting, and the results will be found in the next division.



Recirculator

### Findings

Methane, at atmospheric pressure, was converted in large quantities to ethyne;<sup>1</sup> even after being subjected to the electric discharge for a few minutes.<sup>2</sup> Gilman states that such a free radical reaction might involve charged free radicals.<sup>3</sup> If the electrodes were placed far enough apart to prevent a discharge, the formation of ethyne did not occur.

Ethane was transformed by the discharge into unsaturated hydrocarbons which have not yet been identified.<sup>4</sup>

Tetrachloromethane demonstrated a high dielectric resistance to the electric discharge and decomposed upon the discharge's passage. A simi-

lar decomposition was found in most higher polyhalides.

When methanol in the vapor phase was subjected to a discharge, it was converted in large quantities to methanal. The methanol was recirculated in a continuous cycle from which the methanal was removed by use of a Y-tube.<sup>5</sup> Nonvolatile products accumulated in the flask.<sup>6</sup>

Ethanol vapor was converted in sizable quantities to ethanal when subjected to the same treatment as methanol. Other products were also formed in small, but detectable quantities.<sup>7</sup> Ethanoic acid vapor plus chlorine, when subjected to a discharge in the same apparatus that was used for methanol, formed chlor-

ethanoic acid in quantities large enough to crystallize out of the condensed acid. The control produced barely detectable amounts of chloroethanoic acid.

There is reason to conclude that esterification is retarded by the use of electrodes from an induction coil being placed in the esterifying solution, but this conclusion is premature since further research is needed.

### Correlations to Structure

The reaction by which methane was converted via the discharge to large quantities of ethyne was of a complex nature involving methyl ( $\text{CH}_3\cdot$ ), methylene ( $\text{CH}_2\cdot$ ), and methyne ( $\text{CH}\cdot$ ), radicals, in addition to charged varieties of the same type. A single free radical type reaction mechanism could have produced ethyne, but it seems that the product could have been arrived at by several different, independent free radical reactions although one might have been more efficient in yield than the others. The free radicals could have formed ethane or ethene and probably did in small quantities, but they formed mostly ethyne because of its greater stability under the conditions of the discharge. The triple bond in a carbon-carbon linkage has a higher bond energy than other types of aliphatic C-C linkages<sup>8</sup>. The reaction may be thought of as a rather complex affair of combining free radicals, decomposition of some products, re-formation into different products, but out of these reactions is produced in greatest quantity a more stable compound with respect to the conditions of the discharge.

Because of the density of its chlorine atoms' electron clouds tetrachloro-

methane showed a dielectric resistance to the passage of an electric discharge. Since the tetrachloromethane was decomposed to its elements almost completely when the discharge was forced through it, it might be probable that if a radical such as  $\text{CCL}_3\cdot$  was formed, it might be unstable and decompose shortly after its formation.

In contrast to the tetrachloromethane, trichloromethane showed less resistance to the passage of an electric discharge. This resistance is attributed to the fact that because of the dipole moment (caused by the shift of the electron cloud to the chlorine atoms) the hydrogen atom is left in a vulnerable position. This hydrogen atom would facilitate the ionization of the trichloromethane. In this case the trichloromethane was decomposed into hydrogen chloride, carbon, and chlorine.

The mechanism by which methanol is converted partly to methanal is of a free radical type.<sup>9</sup> Here it is found that the carbonyl group linkage in methanal has a higher bond energy than the carbon-oxygen linkage in methanol. A higher bond energy shows greater stability to cleavage. This discussion does not take into account the association or hydrogen bridge of methanol, but it seems likely this would be broken up by the discharge. It cannot again be said that a single reaction is responsible for the formation of methanal, but one reaction is usually more efficient.

The formation of ethanal from ethanol seems to be of similar nature to the methanol-methanal reaction since again a more stable carbonyl

grouping is formed.<sup>10</sup> This reaction and the methanol-methanal reaction show a similarity of reactions in the lower homologs of the alcohol series.

The formation of chloroethanoic acid from ethanoic acid vapor plus chlorine in a discharge probably does not involve the rupturing of any bonds in the ethanoic acid molecule since ethanoic acid alone is not affected by a discharge.<sup>11</sup> The effect of the discharge in promoting this reaction might involve the cleavage of the chlorine molecule to produce atomic chlorine.

In conclusion, the organic compounds which were subjected to the discharge and were changed, were converted partly by free radical mechanisms into compounds with a more stable configuration in regard to the conditions of the discharge.

#### Continuation of Work

Experiments will be performed to determine the effect of the intensity of the discharge, area of discharge, pressure, etc., on the yield of the product. More complex compounds will be tested, and an attempt to determine the types of free radicals present in reactions will be made. An increase of the yield of ordinary organic reactions and the production of new reactions will be investigated with reference to their application to industry. An electric discharge might become a tool in the petroleum industry for producing better gasoline and new compounds from petroleum products and perhaps even synthesizing gasoline from its elements.

#### NOTES

1. Throughout the context of this paper I.U.C. names will be used.

2. An induction coil with a potential of about 30,000 volts was used. The process, as I later found out, was not a new one. The Germans used it as a process for producing ethyne on a large scale.

3. Gilman, *Organic Chemistry*, Page 616.

4. Lack of proper equipment made the identification difficult, but ethyne from the methane experiment was identified through its silver salt.

5. It was circulated for one and a half hours.

6. See diagram.

7. The ethanal seemed to undergo an aldol condensation which resulted finally in a resin; however, further analysis is necessary. Very small quantities of an oily liquid were produced. More of this liquid is being produced for analysis.

8. Bond energies were obtained from Fieser and Fieser, *Organic Chemistry*, page 1124.

9. See Appendix.

10. See Appendix.

11. See Appendix.

#### APPENDIX

##### Reaction Mechanisms (Theoretical)

It is interesting to note in the following reactions free radicals remove hydrogen from the neutral starting compounds instead of reacting among themselves. This is because the probability of a free radical contacting a molecule of the starting compound is great because of the relative abundance of the starting compound.

#### I

##### Methanol Methanal

The following reaction is based on bond energy. According to this the

carbon-oxygen bond is weakest.

(1)  $\text{CH}_3\text{OH} \rightarrow \text{CH}_3 \cdot + \cdot\text{OH}$   
 (2)  $\text{CH}_3 \cdot + \text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \cdot\text{CH}_2\text{OH}$  (3)  $\cdot\text{CH}_2\text{OH}$  (rearranges with expulsion of hydrogen atom)  $\rightarrow \text{CH}_2\text{O} + \text{H} \cdot$  (4)  $\text{H} \cdot + \text{CH}_3\text{OH} \rightarrow \text{H}_2 + \cdot\text{CH}_2\text{OH}$  (5)  $\cdot\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H} \cdot$  etc.

Since the discharge produces enough energy to disrupt the stronger bonds: (1)  $\text{CH}_3\text{OH} \rightarrow \text{H} \cdot + \cdot\text{CH}_2\text{OH}$  (2)  $\cdot\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H} \cdot$  (3)  $\text{H} \cdot + \text{CH}_3\text{OH} \rightarrow \text{H}_2 + \cdot\text{CH}_2\text{OH}$  (4)  $\cdot\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H} \cdot$  etc.

These are some of the reactions possible.

## II

### Ethanol Ethanal

Based on bond energies: (1)  $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3 \cdot + \cdot\text{CH}_2\text{OH}$  (2)  $\text{CH}_3 \cdot + \cdot\text{CH}_2\text{OH} \rightarrow \text{CH}_3 + \text{H} \cdot + \text{CH}_2\text{O}$  (3)  $\text{CH}_3 \cdot + \text{H} \cdot + 2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_4 + \text{H}_2 + 2 \cdot\text{CHCH}_2\text{OH}$  (4)  $\cdot\text{CHCH}_2\text{OH} \rightarrow$

$\text{CH}_3\text{CHO}$ . This reaction would probably work better as:

(1)  $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3 \cdot + \cdot\text{CH}_2\text{OH}$   
 (2)  $\text{CH}_3 \cdot + \cdot\text{CH}_2\text{OH} \rightarrow \text{CH}_3 + \text{H} \cdot + \text{CH}_2\text{O}$  (3)  $\text{CH}_3 \cdot + \text{H} \cdot + 2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_4 + \text{H}_2 + 2 \cdot\text{CH}_2\text{CH}_2\text{OH}$  (4)  $2 \cdot\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{H}_2 + 2\text{CH}_3\text{CHO}$

Although much simpler: (1)  $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{H} \cdot + \cdot\text{CH}_2\text{CH}_2\text{OH}$  (rearrangement)  $\rightarrow \text{H} \cdot + \text{CH}_2 = \text{CHOH}$  (Hypothetical, rearranges)  $\rightarrow \text{CH}_3\text{CHO}$

## III

### Ethanoic Acid + Chlorine $\rightarrow$ Chloroethanoic Acid

1  $\text{CH}_3\text{CO}_2\text{H} + \text{Cl}_2 \rightarrow \text{CH}_3\text{CO}_2\text{H} \cdot \text{Cl} + \text{Cl} \cdot$   
 2  $\text{Cl} \cdot + \text{Cl} \cdot + \text{CH}_3\text{CO}_2\text{H} \rightarrow \text{H} \cdot \text{Cl} \cdot \text{Cl} + \cdot\text{CH}_2\text{CO}_2\text{H}$   
 3  $\cdot\text{CH}_2\text{CO}_2\text{H} + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H} + \text{Cl} \cdot$   
 4  $\text{Cl} \cdot + \text{CH}_3\text{CO}_2\text{H} \rightarrow \cdot\text{CH}_2\text{CO}_2\text{H} + \text{MCl}$  etc.

# Tomatoes and Gibberellic Acid

by ERIC FRANKLIN EIKENBERRY

Broad Ripple High School, Indianapolis, Ind.

► GIBBERELIC ACID, a hormone of obscurity, has recently been acclaimed for its property of stimulating plant growth. Great interest has developed in the potentialities of this substance with respect to crop production. This hormone is a metabolic product of a soil-borne fungus called *Gibberella fujikuroi* which is the cause of the "Bakanae" disease (or "foolish seedling" disease) of rice seedlings in the Far East and Japan. In this disease, the seedlings grow several times fast-

er than the normal plants, due to the gibberellic acid produced by the fungus. The chemical composition of gibberellic acid is  $\text{C}_{19}\text{H}_{22}\text{O}_6$  (see appendix I).

Gibberellic acid is several times more powerful than the common plant growth hormones, the auxins (e.g. indoleacetic acid). As little as  $10^{-8}$  g has a growth stimulating effect in some cases. It stimulates growth of many common plants, stimulates germination of seeds, re-



► "FOOLISH SEEDLING" DISEASE of Japanese rice seedlings sparked investigations leading to the development of gibberellic acid as a plant growth promoter. Eric Franklin Eikenberry studied effects of gibberellins on tomatoes as part of his 16th Science Talent Search project.

verses dwarfism, and helps break dormancy. Eli Lilly and Company, of Indianapolis, Ind., recently has made limited quantities of gibberellic acid available for research (the source for this experiment), but has not placed it on the market yet because of insufficient knowledge of its mode of action, and toxicity.

The purpose of this experiment was to determine the effects of gibberellic acid on the growth of cultures of tomato root tips. These root tips were grown in an artificial, chemically defined nutrient under sterile conditions. Gibberellic acid was add-

ed to the nutrient and changes in growth rate were measured.

#### Materials and Methods

The methods of White for isolating and maintaining sterile cultures of root tips were followed in this experiment. The nutrient used consisted of a mineral stock, a carbohydrate (sucrose), and a vitamin supplement (see appendix II for complete composition of nutrient). The nutrient was made up in two liter quantities from stock solutions and distributed in 50 ml aliquots to 40 culture flasks which then were autoclaved. The culture flasks were 125

ml pyrex erlenmeyer flasks capped with aluminum foil, and this covered with a 50 ml beaker for protection. Pyrex glass and double distilled water were used throughout to avoid introduction of spurious materials from soft glass and metal containers.

All handling of the cultures was carried out under a dissection hood in a small room. This room was kept closed at all times to reduce dust circulation. Sterile seeds germinated on a piece of moist filter paper in a petri dish provided the root tips. After these had grown, one was chosen from which to start a clone of roots to be used in the experiment. This was done so that all the roots used would be of similar genetic background.

It has been shown that as a tomato root grows, there is no increase in cross sectional area of the root after maturation of the cells. Thus, elongation becomes a good index of growth. Measurements were taken at 24 hour intervals with a plastic rule.\* The configuration of the root could be followed by use of the flexible rule. The cultures were incubated at 31° C to increase growth and provide uniformity in temperature.

The gibberellic acid was prepared as a 0.01% and a 0.001% solution in 70% ethanol. Ethanol was used because: (1) gibberellic acid is more stable in organic solvents than in water; and (2) 70% ethanol provided a bacteriocidal action necessary because gibberellic acid is heat labile

\* The length and weight bear a constant relation to one another. The error introduced by this type of measurement is never more than 10%, and is seldom more than 3%. This error is always negative in value.

and cannot be autoclaved. One tenth ml of the 0.01% solution, or 0.05 ml of the 0.001% solution was introduced into each flask at the time of inoculation, providing, respectively,  $10^{-5}$  g and  $5 \times 10^{-7}$  g per culture.

### Results

Twenty cultures were set up, and these were allowed to grow for four days. Of these, nine were untreated controls; five were given  $5 \times 10^{-7}$  g of gibberellic acid; and the remaining six were given  $10^{-5}$  g of the hormone. Two control cultures died and were withdrawn on the second day. The resulting growth curves were plotted as a graph.

The graph indicated that at no time did the treated cultures grow faster than the controls.

### Discussion

The results indicate that gibberellic acid produces no growth promoting effect on tomato root tip cultures in the concentrations of  $5 \times 10^{-7}$  and  $10^{-5}$  g per 50 ml of nutrient. At the end of three days several of the treated cultures ceased to grow. This might be attributed to: (1) a toxic action by the gibberellic acid; (2) a toxic action by the ethanol in which the gibberellic acid was dissolved; (3) the destruction or use of all the hormone introduced; or (4) a change in the pH of the nutrient. However, this does not preclude the possibility that another concentration of the hormone would stimulate growth. The mode of action of gibberellic acid—whether it causes the affected cells to elongate, or whether it causes the number of cells to increase, or both—has not been definitely established. This could be determined by histo-

logical preparations. The author plans to continue work along both of these lines.

It was found that root tips should be 10 mm long when transferred to fresh nutrient, or death often resulted. Growth reaches maximum near the third day after transfer. At this time, many cultures began to develop branches. The length of these were added to the figure for the main stem when determining growth.

This work could also be applied to cultures of other tissues (e.g. carrot callus, or meristem tissues of other plants). This would result in a more complete picture of the action of gibberellic acid on plant tissue cultures.

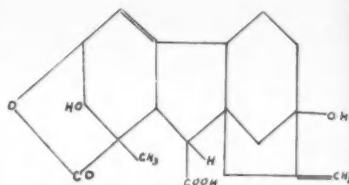
### Summary

A project was begun to determine the effects of a plant growth hormone, gibberellic acid, upon cultures of tomato root tips. Gibberellic acid was introduced into the nutrient of the cultures in concentrations of  $5 \times 10^{-7}$  and  $10^{-5}$  g per 50 ml of nutrient. The cultures treated with gibberellic acid did not grow as rapidly as did the controls. Additional investigation must be conducted to determine the hormone's mode of action, and if another concentration would produce a growth promoting effect. The investigation of the effects of concentration of the hormone is now under way.

For other reports on plant growth promoters, see pages 3, 19, and 28. (Ed.).

### Appendix I

Gibberellic acid is a tetracyclic dihydroxylactonic acid with a composition of  $C_{19}H_{22}O_6$  and the following structural formula (tentative):



Gibberellic acid is soluble in methanol, ethanol, acetone, ether, and water. As a mono-carboxylic acid it will dissolve in sodium bicarbonate and sodium acetate solutions. It is stable in organic solvents, stable in water solutions at room temperature for short periods of time; and unstable at 50° C.

### Appendix II

#### White's Nutrient

White's plant tissue nutrient consists of a mineral stock, a vitamin supplement, and a carbohydrate. The mineral stock consists of:

Ca(NO <sub>3</sub> ) <sub>2</sub> .....	20	g
Na <sub>2</sub> SO <sub>4</sub> .....	20	g
KNO <sub>3</sub> .....	8	g
KCl .....	6.5	g
NaH <sub>2</sub> PO <sub>4</sub> .....	1.65	g
MnSO <sub>4</sub> .....	0.45	g
ZnSO <sub>4</sub> .....	0.15	g
H <sub>3</sub> BO <sub>3</sub> .....	0.15	g
KI .....	0.075	g

These are dissolved, one at a time, in 8 liters of double distilled water. If any of the above salts is used as a hydrate, the weight correction must be made. Thirty-six grams of MgSO<sub>4</sub> are dissolved separately in 2 liters of water. These two solutions are then slowly mixed in a 10-liter serum bottle. This mineral stock is ten times the concentration used in the completed nutrient. The vitamin supplement consists of 300 mg glycine, 50 mg nicotinic acid, 10 mg thiamine, and 10 mg pyridoxine dissolved in 100 ml of water. This stock is 1000 times the concentration used.

Two liters make a convenient amount of nutrient. Forty grams of C. P. sucrose are dissolved in one liter of water. To this is added 5 mg Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 200 ml stock salt solution, and 2 ml vitamin supplement, and the whole is made up to 2 liters. This is distributed and autoclaved.



# Auxin and a Climbing Plant

by ROBERT E. GOLDSTEIN

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## Introduction

► TWO PRIMARY BIOLOGICAL life functions are the growth of an organism, encompassing both physical increase in size and maturation of the reproductive system, and adaptation of an organism to its environment. In plant life nature has vested the control of these vital functions in one single organic compound, indole-3-acetic acid, or auxin, as it is more commonly called.

Auxin is produced in the apical meristem (or apex), young leaves, and unripe fruit. From the tip auxin flows to all parts of the organism, much as hormones circulate in animals. Auxin, however, exhibits a strange polarity; it cannot flow upwards towards the tip where it originated. Auxin governs the expansion of all young, active cells. It causes elongation of the stem by stimulating growth in internode areas and lateral growth by stimulating the cambium. Also auxin retards bud development. When the amount of auxin decreases in a leaf or fruit, the affected part is shed. Small quantities of auxin seem to stimulate root development in the pericycle, but large amounts of auxin retard the growth of roots. Likewise, a small amount of auxin stimulates the production of flowers, but large amounts retard flowering. Auxin is present in relatively large quantities during and after fertilization in both the ovary and live pollen. This auxin regulates and harmonizes the development of the entire plant.

The exact role of this plant hormone as a growth regulating mechanism in a certain local weed seemed to present a problem worthy of scientific investigation. The weed, *Cynanchum vincetoxicum*, or black swallowtail, grows profusely in the Rochester area during the late spring and summer. It grows rapidly, tangling its single stem around a host plant and sending an extensive root system into the earth. The plant can and does propagate in bright sunlight or deep shade, but it does best in moderate shade. Rapid growth, regeneration, and vegetative propagation make the plant flourish and spread profusely. The purpose of this project is to determine how auxin influences stem elongation and thigmotropism in *Cynanchum vincetoxicum*.

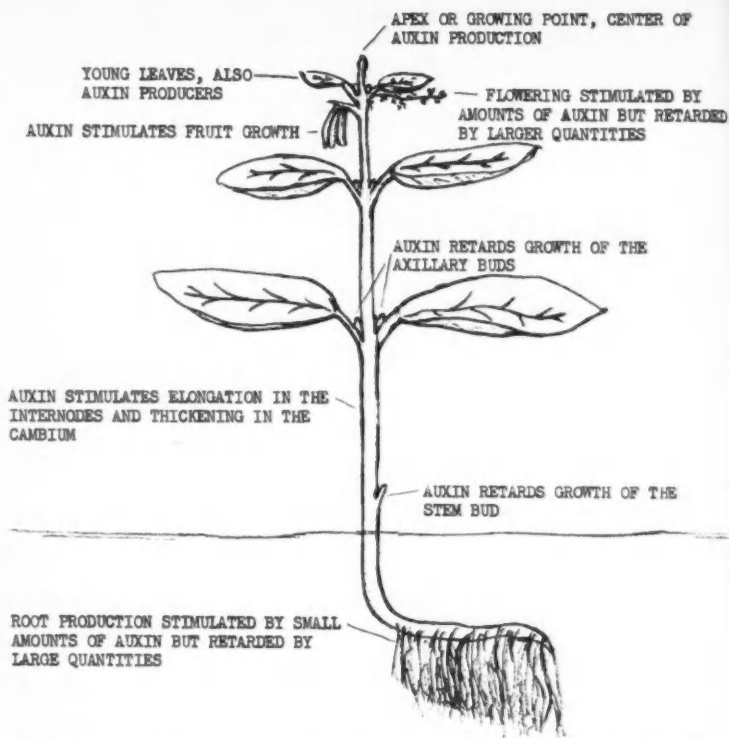
## Problem and Hypothesis

After a preliminary survey I formulated the following four specific questions:

1. Is auxin present in the growing parts of the plant?
2. Is auxin produced by the apex or young leaves responsible for suppressing growth of the auxiliary and other buds?
3. Is auxin responsible for elongation of the stem?
4. Is thigmotropism affected by the removal of auxin-producing areas?

To answer these questions I devised a series of experiments:

1. To determine whether auxin is



➤ *GROWTH-PROMOTING AUXIN is produced in the apex and young leaves of plants as shown here, as well as in unripe fruit. From the production centers it spreads to nearly all parts of the plant.*

present, I would test equal weights of crushed stem, leaf, and stem apex tissue with a suitable qualitative reagent.

2. To investigate the relationship between the apex and the young leaves I would cut off the apex and/or the young leaves of several groups of plants in varying patterns. Several plants would be used as controls. Bi-daily measurements of the

stem length would be taken, and stakes would be used to gather data to answer question four.

3. To investigate stem elongation I would cut off apices of several plants and replace them with a lanolin and auxin paste. Several concentrations of auxin would be used, including zero, and a group of plants would remain untouched as a control. Bi-daily measurements of each

internode would be taken. Stakes would be used to obtain data for question four.

Because the plant grows so rapidly, I thought that readily detectable amounts of auxin would be present in the growing parts and that this auxin would be found responsible for stem elongation. Because the plant sends up only one single stem, i.e., it exhibits strong apical dominance, I anticipated finding that auxin suppresses the growth of apical buds. If these assumptions proved true, I expected to find that auxin stimulates thigmotropism, because the thigmotropic reaction is a change in the nature of stem growth.

#### *Experimental Procedures*

On July 1, I gathered 75 healthy plants from a local field and potted them in sandy greenhouse soil. In order to provide uniform growth conditions, facilitate transportation, and minimize water loss, I cut all the plants off above the first pair of leaves. Experimental data were furnished by the dominant axillary bud which grew as a result of this abscission. Five plants were placed in each pot, since each part of experiments two and three was to be replicated five times. Every pot was given a number, and every plant a letter.

After sixteen days all but two plants produced axillary development averaging about 6.5 mm. I prepared pots one through six for experiment two and used the resulting apex and leaf tissue for experiment one. Stem tissue was obtained from pot seven.

#### *Experiment 1*

Equal weights of each tissue sample were ground with water in

a mortar with washed sand, and centrifuged for 30 minutes at 10,000 r.p.m. Auxin, a water soluble compound, remained in the liquid part of the sample. Salkowski's reagent ( $\text{FeCl}_3$  and  $\text{H}_2\text{SO}_4$ ) was added to this fluid extract. Isopropanol was also added to intensify the results. A mixture of Salkowski's reagent and isopropanol was kept for control purposes. Within 48 hours all of the samples turned from the greenish-yellow of the reagent to a light pink, indicating the presence of a substantial amount of auxin. (This test is not a sensitive quantitative test.)

#### *Experiment 2*

By July 16 most plants had produced one pair of mature leaves and one pair of young leaves. On this day the various plant parts were removed, and two pots were treated with lanolin paste. Bi-daily I recorded measurements of the main axillary stem growth, secondary axillary stem growth, and the sum of the growth of stem buds and axillary and stem buds on the previously mentioned stems.

From my experimentation I observed the following:

1. Growth of the main stem was greatest when the auxin-producing parts remained intact.

- A. Growth of the main stem was much greater in plants retaining their apices than in those with the apices cut off.

- B. Growth of the main stem was slightly greater in plants retaining both apex and (young) leaves than in those with just the apex.

- C. Growth of the main stem was about the same when plants retained just the leaves and when

they retained neither apex nor leaves.

2. When the main stem apex was removed, the plants retaining the leaves experienced greater growth of the subsidiary stem and lesser buds than those without the leaves.

3. Growth of the subsidiary axillary stem and lesser stem and axillary buds eventually compensated for the loss of the main stem apex.

4. When auxin was substituted for a growing part, growth was temporarily maintained.

A. When all auxin producing parts were removed, plants treated with auxin temporarily grew more than those untreated, and retained apical dominance, while those untreated did not.

B. The plant which retained its main stem apex but whose leaves were replaced by auxin grew about as much as a plant retaining both apex and leaves.

5. Lanolin did not produce the same effect as one per cent auxin in lanolin.

Ten days after the experiment began, an unfortunate accident halted the experiment. Growth increment was steadily declining in all plants, and many leaves became mottled with lighter green, indicating a deficiency of necessary mineral salts. To compensate I added organic fertilizer, but I grossly overestimated the plants' needs. As soon as I realized my mistake, I removed the fertilizer burn which rendered the plants incapable of normal growth. (A fertilizer burn is the rapid loss of water in a plant caused by an excess of soluble salts in the soil water.) However, I made several informal observations which I record here:

1. Growth was halted in all plants; some of the larger plants regressed.

2. Those plants which grew the most regressed the most.

3. Regression was greatest in the youngest parts.

### Experiment 3

To carry out experiment 3, I discarded the burned greenhouse plants and began to experiment outdoors. Since I suspected that the greenhouse plants were adversely affected by light conditions, I arranged my experiment to include an investigation of the effect of light on plant growth. In the area where I obtained the greenhouse plants, I selected five groves of *Cynanchum vincetoxicum* varying in light intensity from bright sun to deep shade. One replication grew in each grove. I devised a banding system with plastic tape to identify the plants, and cut off the tops of each plant in the same way as the greenhouse plants had been cut. Negative results were obtained because of unseasonably cold weather; none of the axillary buds grew more than 1 cm.

### Conclusions

From my experiments I have concluded:

1. Growth and apical dominance in *Cynanchum vincetoxicum* is caused by indole-3-acetic acid produced in the apex and young leaves of the plant.

2. The greatest amount of auxin in *Cynanchum vincetoxicum* is produced by the apex, although the young leaves produce significant quantities.

3. *Cynanchum vincetoxicum* grows very profusely in spite of the loss of

its apex, because this loss is rapidly compensated by the development of numerous small buds.

4. When auxin paste is being applied to the cut surface of a plant for experimental purposes, the paste should be renewed daily.

#### *Future Experiments*

Some interesting avenues of inquiry resulting from my research may be:

1. What are the optimum conditions, physical and chemical, for the growth of *Cynanchum vincitoxicum*?

2. A large amount of auxin ap-

peared to inhibit bud development, but a small amount seemed to encourage it. Is this true?

3. After the plants were burned by fertilizer, the area containing auxin seemed to lose the most water. Is this true? Is this possibly a new way to study the role of auxin in plant metabolism?

These questions would probably make interesting subjects for future experiment.

*For other reports on plant growth promoters, see pages 3, 15, and 28. (Ed.).*

## **Effect of Metal Compounds on Natural Rubber**

by JEFFREY SYDNEY HANOR

*Arlington Heights Township H. S., Arlington Heights, Ill.*

➤ IT IS WELL KNOWN that natural rubber, or isoprene, is affected in either solution, dispersion, or dry form by various metal compounds. Copper, cobalt, manganese, and iron in concentrations greater than five parts per million have the greatest effect in the deterioration of natural rubber. Other metals such as lead, mercury, and cerium affect the rubber to various degrees.

#### **Viscosity Measurements**

All of these metal compounds or ions are oxidation catalysts. Natural rubber polymerizes into chains containing about 14,706 isoprene molecules. These various metal compounds tend to break up the large rubber molecule into smaller parts or free radicals which are free to unite with oxygen, thus forming smaller

molecules. This reduction in molecular weight causes a decrease in the plasticity and solution viscosity of the rubber. By measuring the solution viscosity, or resistance to flow, of the rubber, it is possible to determine the rate and amount of oxidation.

Many styles of viscometers have been developed to meet many specific needs. However, the most readily accessible viscometer for my purpose was the Brookfield Syncro-Lectric Viscometer. This viscometer measures the drag induced upon a spindle rotating at a definite, constant speed while immersed in the test material. The drag is indicated on a rotating dial by a pointer which is attached to the spindle shaft and represents the tension produced on a spiral spring. The core of this spring



► COBALT AND MANGANESE NAPHTHANATE were found by Jeffrey Sydney Hanor to increase the viscosity of natural rubber.

is fastened to the spindle shaft; and the outside coil terminal, to the dial which is directly connected to the motor shaft.

#### Experimental

In this experiment I used a standard rubber solution. A set amount of this solution (about 400 grams) was poured into a can of standard size. Then I added the compound under consideration, ten parts of additive to one million parts of rubber solution, so that I would always have the same amount of additive in proportion to the amount of rubber solution. The compound was either introduced into the rubber directly, or suspended or dissolved in an inert solvent. The rubber and additive were then mixed

by means of an electric whip in order to combine them. When rubber is whipped, it becomes much less viscous. This phenomenon is known as thixatropy. To insure that the thixatropy would not ruin the first reading, I whipped the rubber just before each successive reading to be consistent. The can was then subjected to a water bath of 24° C. so that a constant temperature could be maintained. The viscosity reading was then taken, and the can sealed. Detailed records were kept on the initial weight of the rubber and solvent, the weight of the additive, the viscosity reading, and the date of the reading.

In order to maintain a constant solid content, all bits of rubber left on the whip and viscometer were put back into the test can. At the succeeding viscosity readings, the weight of the rubber and solvent was found and subtracted from the initial weight of the rubber and solvent. I could then compute how much solvent had evaporated and add that amount back into the test can. Because I had lost no rubber and had added the solvent lost, I still had the same percentage of rubber and solvent. Thus, everything was controlled except the viscosity reading, which was taken weekly.

The designation of the rubber used throughout the experiment was:

10% solution of RSS #1  
Smoked Sheet solution in  
petrolene  
Source of RSS, Indonesia  
Mooney of RSS, 73

The Mooney is the unit of measurement of the plasticity of the dry rubber. About midway in my experiment, a new drum of rubber was obtained which had either a slightly

higher Mooney reading or solid content. Although the average viscosity was raised, I was primarily concerned with the relative amount of drop in viscosity.

In the course of experimenting, I tested seventeen metal compounds, focusing my attention on the cobalt, copper, iron, and manganese compounds. I have numbered each compound in the order in which it was tested, as is indicated in Table I.

In this report the above chemicals will be referred to by their respective number.

Table II indicates the viscosity readings obtained over a period of four weeks. From this table I prepared graphs of the viscosity change. In this report all viscosity readings are in centipoises, where the viscosity of water at 20.20° C. is equivalent to one centipoise.

The rubber industry is primarily interested in the rate at which the

rubber is oxidized, as rapid oxidation can cause spontaneous fires, and slightly slower oxidation can cause rapid deterioration of rubber products. For the majority of compounds, the most rapid oxidation occurred during the first two weeks of testing. The oxidation then tended to slow up considerably during the fourth week, although it did not cease completely.

In analyzing the data, I found that the highest rate of oxidation for each compound provided an excellent means for comparing the effects of the compounds. I found that this highest rate of oxidation was roughly proportional to the average rate of oxidation and to the total amount of oxidation over the period tested. Since the highest rate of oxidation could be computed the most accurately, I used it in my comparisons.

The steepest portion of each curve, obtained from plotting data as a

TABLE I — COMPOUNDS TESTED

NUMBER	COMPOUND
1	cobalt hexamethylenetetramine
2	copper diethyl dithiocarbamate
3	cobalt naphthanate
4	manganese naphthanate
5	ferrous sulfate
6	ferric chloride
7	ferric oxide
8	cobalt chloride
9	cupric chloride
10	cupric acetate
11	cuprous chloride
12	manganous chloride
13	manganese dioxide
14	aluminum sulfate
15	nickel ammonium sulfate
16	lead acetate
17	ammonium chloride

TABLE II — VISCOSITY READINGS

COMPOUND	READINGS:	1	2	3	4	5
1		6200.0	6000.0	5100.0	5100.0	5000.0
2		6700.0	6250.0	5600.0	5300.0	5050.0
3		5150.0	6300.0	5850.0	5500.0	5400.0
4		5100.0	5250.0	5400.0	5100.0	4900.0
5		17,500.0	10,000.0	12,800.0	11,600.0	11,500.0
6		8550.0	8200.0	7500.0	7100.0	
7		9650.0	8600.0	7800.0	7500.0	
8*		17,500.0	15,500.0	14,500.0		
9		14,200.0	14,500.0	13,000.0		
10		13,800.0	13,000.0	**	9500.0	
11		19,500.0	16,250.0	15,000.0		
12		18,500.0	16,260.0	15,500.0		
13		20,000.0	18,000.0	17,000.0		
14		21,500.0	18,750.0	17,500.0		
15		21,000.0	18,500.0	17,500.0		
16		19,000.0	15,250.0	13,500.0		
17		22,000.0	19,500.0	18,500.0		

\* Starting with can number 8, the second drum of isoprene was used.

\*\* Data lost.

graph, was very nearly a straight line. Assuming it to be such, I divided its distance along the viscosity axis by its distance along the time axis, thereby obtaining the highest rate of oxidation for each compound. Table III lists the compounds according to the rate of oxidation. The total oxidation is given for comparison, but it must not be considered as conclusive, as several of the compounds were tested over shorter periods.

The copper compounds are notable exceptions to the regularity of the Total Oxidation column, usually having high total oxidation readings. This suggests extensive deterioration.

Being primarily interested with the Cu, Co, Mn, and Fe compounds, I computed their respective oxidation averages from Table III. I found that copper compounds have the greatest effect on the rubber. This result checks with copper's effect on total

oxidation. Manganese is the next destructive, followed by cobalt and iron in that order.

COMPOUNDS	OXIDATION RATE
copper .....	325.0
manganese .....	260.0
cobalt .....	183.2
iron .....	140.0

In computing the oxidation average for iron, I did not include the results for ferrous sulfate. Its great undulations suggest that it is causing reactions of far greater complexity than oxidation. Specialized research will have to be done with ferrous sulfate.

Besides the Cu, Mn, Co, and Fe compounds, I tested several other metals. However, since only one compound of each metal was tested, averages could not be computed. Instead, I tried to determine if the negative



TABLE III — THE EFFECTS OF THE METAL COMPOUNDS

COMPOUND	HIGHEST RATE OF OXIDATION <i>Centipoises per day</i>	TOTAL OXIDATION <i>Centipoises</i>
ferrous sulfate	1200	6000
lead acetate	740	5500
aluminum sulfate	600	3500
cuprous chloride	560	4000
ammonium chloride	500	3250
nickel ammonium sulfate	500	3500
manganese chloride	400	3000
copper acetate	370	4300
manganese dioxide	340	3000
cobalt chloride	340	3000
cupric chloride	270	1200
ferric oxide	160	2150
cobalt hexamethylenetetramine	140	1200
ferric chloride	120	1650
copper diethyldithiocarbamate	120	1650
cobalt naphthanate	70	900
manganese naphthanate	40	100

radicals had any characteristic effect. The acid salts, sulfates, chlorides, and acetates, had a much greater effect in oxidizing the rubber than did the oxides and organic compounds. Acid salts, for the most part, ionize very readily, but most oxides and organic salts show extremely weak ionization. This seems to indicate that metal *ions* as catalysts have a greater effect in deteriorating the rubber than do metal *compounds* which do not ionize. The ion is perhaps freer to come into contact with the rubber molecule, thereby causing oxidation. More experimenting will have to be done to give positive verification to this conclusion.

The data seems to indicate that the naphthanates have a characteristic

effect on the rubber. Both cobalt and manganese naphthanate increased the viscosity of the rubber until it reached a peak one or two weeks after the initial reading. The viscosity then dropped off slightly.

In this paper I have outlined my experiment and have stated my results and conclusions. I believe that the rubber industry may find these results and conclusions of some use in knowing which metals are especially harmful to the rubber and rubber products. The data on the particular compounds tested should be of some value. The results also seem to indicate that there is a definite relationship between the ionization of the catalyst and the oxidation of the rubber.

# Synthetic Plant Growth Hormones

by DOROTHY ANITA HOLLINGSHEAD  
*Murphy High School, Atlanta, Ga.*

► SINCE 1907 it has been a proven fact that animal hormones exist and that these hormones exert a definite and profound effect on the growth and processes of the animal body. However, it was 1928 before it was definitely proved that a hormone or regulator occurred in plants. The plant hormone was called an auxin and initiated the research that has resulted in new theories and possibilities.

## Historical

The history behind this year of proof began in 1880 with Hest, who suggested that there was a migratory growth substance in plants. This was the first time the idea of a plant hormone had been presented. Two years later, in 1882, Julius Sachs stated after much research that specific substances correlated the activities of plants by directing the activities of cells, and that plant activity was not determined by nutrients. Until 1928, when Went of the University of California began his experiments, these theories remained relatively untouched. Since 1928, auxins have been isolated for use from germinating seeds, developing shoots, and even inactive seeds and pollen grain. Also a number of organic acids have been found to possess growth regulatory properties similar to those of auxins. These include indolepropionic, indolebutyric, naphthaleacetic, and indoleacetic acids. It is with the investigation of these chemicals that a great possibility for advance in plant culture lies.

## Plant Hormone Activity

Hormones are substances synthesized within an organism which in very minute concentrations exert profound effects on its metabolism and growth, usually after translocation to parts or organs remote from their centers of production.

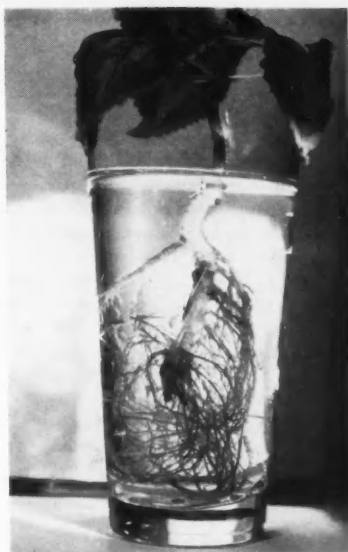
Went investigated the actions of these plant hormones in the coleoptile of an oat (a cylindrical structure several centimeters in height. It encloses the first leaf.) If the tip of an oat coleoptile is removed, Went discovered, the elongation of the stump is greatly retarded, almost stopped. If, however, the coleoptile is replaced, the usual rate of elongation is resumed. Went also found that if, when the coleoptile was removed, it was placed on a small agar block, the agar block will have the same effect as the coleoptile when placed on the stump. These facts indicated that the tip exerts a controlling influence on the elongation of basal cells. This influence is contributable to some diffusible substances which move from the tip toward the base. These substances we call auxins.

The effect of growth regulators depends on the concentration. It may stimulate mitosis or elongation or it may initiate the formation of adventitious roots. Auxins are involved in response to light, healing of wounds, development of fruit, leaves, and roots. The transport of auxins is strictly longitudinal. Their movement bears a close resemblance to protoplasmic or chloroplastic streaming.

There can be no doubt as to the importance of plants for our lives. Our very existence requires them, for plants alone can manufacture the food our bodies demand. It is quite true, then, that methods for increasing the speed and successfulness of rooting, elongation, fruit-bearing, and all other auxin-influenced activities could be most beneficial in our agricultural future. Commercial gardeners, florists, farmers, and home gardeners could get two crops, perhaps, from the same land that previously yielded one. A better quality plant could be produced due to the increased production of fruit and foliage. The possibility of bigger and better crops would be greatly increased by chemical growth regulators which could influence all the facets of the plants' development.

#### Experimental Method

The aim of my project was, essentially, to ascertain a solution of a chemical which would function as a synthetic plant hormone in accelerating root production. In order to set up a practical experiment in which results could be easily observed and one which could be handled easily on a large enough scale for those results to be accurate, I selected coleus vulgaris, a plant which roots quickly and abundantly from cuttings under favorable conditions. The chemical used was indoleacetic acid in solutions ranging from .05 parts per million to 10 parts per million. These solutions were prepared by weighing crystalized indoleacetic acid on an analytical balance in amounts that were proportionate to 10 liters of water (distilled) in order to produce the proper concentrations. These solu-



➤ *TWO AND ONE-HALF PARTS per million of indoleacetic acid were found by a Science Talent Search winner to effectively stimulate root production in this member of the mint family.*

tions were stored in large well sealed bottles between periods of use.

Six seed flats, 1' x 1½' x 3½'', were obtained. Three of these were filled with commercial Vermiculite and the other three with a medium-coarse silica sand. As the sand was procured at a construction concern, it was sterilized in a pressure-heating device to remove possible impurities. Forty small cuttings of coleus vulgaris were obtained and cut at an approximate angle of 45° just below a leaf node. The cut tips of these coleus cuttings were soaked for twenty-four hours in labeled test tubes containing the var-

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ious solutions. These were then planted, six to a box and labeled carefully with tongue depressors. The cuttings were stored in a small greenhouse with east-west light.

It was kept at an approximate temperature of 50°-65° with an average temperature of 58°. To prevent excessive transpiration a double thickness of cheesecloth was kept over the flats at all times. The cuttings were watched closely and regularly; *all* changes were noted and recorded. The silica sand dried rapidly and required more attention and frequent watering than the vermiculite which absorbed water and held it for a long time. It was difficult to judge how moist the vermiculite was, but usually it could be determined by feeling with the back of the hand or by crushing a small particle of it between finger and thumb. The rooting medias were kept fairly moist at all times with regular tap water. *No nutrients* were supplied during the entire period of the experiment, for the object of the whole endeavor was concerned with auxin-controlled plant activities which are completely independent of nutrients.

After the fourth week my first main problem occurred. A white, filmy mold (unidentified) began to spread over the vermiculite and was threatening the plants. Its first appearance was in little patches which were easily removed. However, the mold returned and continued to spread. There was no apparent cause or remedy for the blight, and even

my consultants could offer no specific instructions. A commercial spray-type fungus killer was used on the medium and it quickly disappeared. To prevent its return and also to facilitate care and observation, I undertook to build several small greenhouses to house the flats at my home. These were constructed from a heavy wire framework covered with polyethylene sheets. The polyethylene was attached with thick black plastic tape. These artificial greenhouses served very well. They accomplished two things: (1) Regulated satisfactorily the moisture content of the air, and (2) provided for the maintaining of a constant temperature at my home.

#### Conclusion

The roots were checked about every four days. Daily records were kept from which charts were compiled.

It would appear that a safe conclusion from these experiments would be this: A certain concentration of indoleacetic acid would prove most effective in serving as a synthetic growth hormone and will greatly accelerate root production in the coleus vulgaris. The experiments indicate that a concentration of 2.5 parts per million is an effective solution in the previously mentioned capacity. Further experiments could lead to discoveries of potential power in agricultural progress.

*For other reports on plant growth promoters, see pages 3, 15, and 19. (Ed.).*

Pipelines are now by far the most important method for transporting crude oil, much of it going by trunklines to refineries.

Sometimes up to 60% of the stalks in an irrigated corn field break before harvest.



► MOLYBDENUM COMPOUNDS prepared by Dean Carl Luehrs as demonstrated during the 16th Science Talent Institute.

## Molybdenum Compounds

by DEAN CARL LUEHRS

Everett High School, Lansing, Mich.

► WHILE READING a book on the chemistry of molybdenum, I became impressed by the vast amount of information that was either not known or else known with but little degree of exactness. Different workers would contradict each other, and no one seemed to have a complete explanation of such phenomena as polymerization of anions to form isopolymers and heteropolymers. I decided to in-

vestigate the chemistry of molybdenum for myself.

### Molybdates

First, I tried to learn some of the general chemistry of molybdenum, starting with the molybdates. This series of compounds is similar to the sulfates and resembles the chromates even more. For instance, the order of increasing solubility: barium, strontium, calcium, and magnesium, holds

true for the molybdates as well as the sulfates and chromates. Table I describes the molybdates I prepared.

Related to the molybdates are the thiomolybdates in which one or more oxygen atoms of the molybdate ion are replaced by sulfur atoms. These compounds may be formed by the reaction of a soluble sulfide or hydroxide with molybdenum trisulfide or by the reaction of a soluble sulfide with molybdenum trioxide.

I prepared  $\text{Na}_2\text{MoO}_3\text{S}$ , which gave a yellowish-brown solution, by dissolving molybdenum trioxide in sodium sulfide. This was not a simple reaction because some molybdenum blue was left undissolved, indicating that a certain degree of reduction of the molybdenum had taken place. Other monothiomolybdates were prepared by double decomposition (see table II).

$\text{K}_2\text{MoO}_2\text{S}_2$  may be prepared by the reaction of potassium trimolybdate and potassium sulfide.<sup>1</sup> I tried to prepare it by dissolving molybdenum dioxide in sodium polysulfide and also by dissolving molybdenum disulfide in sodium peroxide. Neither of these attempts were successful.

I prepared  $\text{Na}_2\text{MoOS}_3$  by dissolving molybdenum trisulfide in sodium hydroxide. I made the molybdenum trisulfide by bubbling hydrogen sulfide through a solution of a molybdate acidified with sulfuric acid. Hydrochloric acid is not satisfactory because it tends to reduce the molybdenum, and the net result is a beaker full of molybdenum blue. In any valence, molybdenum is extremely sensitive to changes in redox potential.

Cherry red  $\text{Na}_2\text{MoS}_4$  was prepared by dissolving molybdenum trisulfide in sodium sulfide. This com-

pound is susceptible to oxidation by the air, because after the solution had stood for a few days, yellow particles of sulfur formed, and the solution changed to a yellow-brown color similar to  $\text{Na}_2\text{MoOS}_3$  or  $\text{Na}_2\text{MoO}_3\text{S}$ .

Molybdenum dioxide can be prepared by heating ammonium paramolybdate. Complete reduction does not take place unless every particle is heated red hot. This compound is not too reactive. Molybdates are formed when molybdenum dioxide is heated with sodium hypochlorite solution or with potassium chlorate.

When a solution of ammonium paramolybdate in concentrated hydrochloric acid is electrolyzed, an intensely green solution results. This compound is molybdenum trichloride.<sup>2</sup> When this solution was saturated with ammonium chloride, a brick red precipitate formed. This is supposed to be  $(\text{NH}_4)_2\text{MoCl}_5 \cdot \text{H}_2\text{O}$ .<sup>3</sup> This gives a cream colored precipitate with mercuric chloride and a light yellow one with copper sulfate. The addition of potassium bromide to the green solution gives a brown solution, probably  $\text{K}_2\text{MoBr}_5$ . Reducing a concentrated sulfuric acid solution of ammonium paramolybdate in a similar manner gives an intensely blue solution.

#### Qualitative Tests

A thiocyanate added to one of these trivalent halide solutions will produce an intensely red color. This color may be extracted with ether. A different red colored complex is formed by reducing a hydrochloric acid solution of a molybdate with stannous chloride and then adding the thiocyanate. At Michigan State University, where I worked last sum-



mer, the red color is extracted with isoamyl alcohol, and the color estimated colorimetrically. The molybdenum content of a sample can be determined even if it is only a few parts per million. Although this compound is used in analysis, its exact constitution is not known. It is known, however, that the ratio of thiocyanate to molybdenum is three to one, and that the molybdenum is quinquivalent.<sup>4</sup> Potassium cyanide will form similar complexes.

Another sensitive test for molybdenum is the xanthate test. Potassium hydroxide and carbon disulfide are dissolved in ethyl alcohol, and acetic acid is added. When a solution containing molybdates is added, a lavender color forms. Nitric acid will intensify the color and assure that the molybdenum is not reduced. The color may be extracted with ether, thus making the test more sensitive. I got a strong color in the ether with less than two hundred parts per million of molybdenum.

I added lead acetate to a solution of a molybdate, chromate, and sulfate. An orange precipitate formed, which was a completely different color than the ordinary yellow lead chromate. The usual rhombic crystals of lead chromate, by the influence of tetragonal lead molybdate, change to the tetragonal crystal form which is red.<sup>5</sup> This pigment has considerable covering power.

Molybdenum forms a great variety of complex acids in which it is polymerized to form anions of great size. In an acid solution, it is believed that isopolymers containing two to six molybdenum atoms condense with another acid to form a complex which may have a molecular weight as high

as one or two thousand.<sup>6</sup> The most important of the complexes with phosphoric acid,  $\text{H}_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot x\text{H}_2\text{O}$ , is useful in determining the amount of phosphates in a sample. Ammonium phosphomolybdate is insoluble in nitric acid, and the yellow precipitate may be compared with a standard. Another method is to reduce the phosphomolybdate to molybdenum blue and estimate the color colorimetrically.

Oxalic acid forms a complex with molybdenum which crystalizes in translucent parallelepipeds. Yellow silicomolybdates may be prepared by adding hydrochloric acid to a solution of a molybdate and silicate. A light yellow color forms when either tartaric or salicylic acid is added to an acidified molybdate solution, indicating that complex acid formation is taking place. Hot tannic acid solution and molybdic acid give a ruby colored solution.

## II

The green reduced hydrochloric acid solution of a molybdate and the blue reduced sulfuric acid solution of a molybdate each give a light brown solution when diluted. This leads me to believe that a complex acid is formed. Twelve normal hydrochloric acid solution of a molybdate will give a red solution when reduced electrolytically<sup>7</sup>, and the less highly acidified solutions, the green color. Perhaps the red solution is  $\text{H}_3\text{MoCl}_6$ ; the green,  $\text{H}_2\text{MoCl}_5$ ; and the light brown solution,  $\text{MoCl}_3 \cdot \text{MoCl}_5 \cdot 3\text{H}_2\text{O}$  is copper colored. My green solution gave brick red  $(\text{NH}_4)_2\text{MoCl}_5$  when saturated with ammonium chloride. A red solution might give rose red  $(\text{NH}_4)_3\text{MoCl}_6$ .

### III

My work is still in its embryonic stages. I am just beginning to discover some of the intriguing problems of molybdenum chemistry. My next step is to prepare a red solution of molybdenum trichloride and see if my hypothesis is valid.

Since the chemistry of element forty-two is so involved, it offers a wide field for the researcher. The readiness with which it changes valence states and the tendency to form complex ions combine to keep the researcher on his toes whenever he encounters molybdenum compounds in his work.

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TABLE I — MOLYBDATES

$\text{Al}_2(\text{MoO}_4)_3$	white pp.	sol. in HCl
$(\text{NH}_4)_2\text{MoO}_4$	add $\text{NH}_4\text{OH}$ to ammonium paramolybdate	loses $\text{NH}_3$
$\text{Sb}_2(\text{MoO}_4)_3$	yellow white pp.	sol. in HCl
$\text{BaMoO}_4$	white pp.	sol. in HCl
$\text{Bi}_2(\text{MoO}_4)_3$	yellow pp.	slightly soluble, is completely soluble in HCl
$\text{CdMoO}_4$	white pp.	soluble in HCl, KCN, $\text{NH}_4\text{OH}$
$\text{CaMoO}_4$	white pp.	sol. in HCl
$\text{Cr}_2(\text{MoO}_4)_3?$	heat an excess of $\text{Cr}(\text{OH})_3$ with ammonium paramolybdate, a green solid forms, part of it dissolves	light brown solution contains chromic and molybdate ions
$\text{CuMoO}_4$	light green pp.	sol. in HCl, $\text{NH}_4\text{OH}$
$\text{Fe}_2(\text{MoO}_4)_3$	yellow-brown jelly	sol. in HCl
$\text{PbMoO}_4$	white pp.	sol. in $\text{HNO}_3$
$\text{LiMoO}_4$	heat an excess of $\text{LiNO}_3$ with ammonium paramolybdate	white salt, sol. in $\text{H}_2\text{O}$
$\text{MgMoO}_4$	heated $\text{MgO}$ with ammonium paramolybdate	sol. in $\text{H}_2\text{O}$
$\text{MnMoO}_4$	light yellow pp.	sol. in HCl
$\text{HgMoO}_4$	yellow pp.	sol. in HCl

Hg <sub>2</sub> MoO <sub>4</sub>	bright yellow pp.	sol. in HNO <sub>3</sub>
NiMoO <sub>4</sub>	light green pp.	sol. in HCl
Ag <sub>2</sub> MoO <sub>4</sub>	white pp.	sol. in NH <sub>4</sub> OH and KCN
Na <sub>2</sub> MoO <sub>4</sub>	add NaOH to ammonium paramolybdate	white salt
SrMoO <sub>4</sub>	gelatinous white pp.	sol. in HCl
ZnMoO <sub>4</sub>	gelatinous white pp.	sol. in HCl and NH <sub>4</sub> OH

All of the preceding compounds were made by double decomposition with sodium molybdate unless stated otherwise.

#### OTHER MOLYBDATES

(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> · 4H <sub>2</sub> O	commercial compound of molybdenum - "molybdic acid, 85%"	
Ba <sub>3</sub> Mo <sub>7</sub> O <sub>24</sub> · 9H <sub>2</sub> O	prepare by double decomposition	sol. in HCl
Co <sub>2</sub> O <sub>3</sub> · 7MoO <sub>3</sub> · 5NH <sub>3</sub> · 3H <sub>2</sub> O	CoCl <sub>2</sub> and NH <sub>3</sub> , then H <sub>2</sub> O, then ammonium paramolybdate	rose colored crystals
Cu(NH <sub>3</sub> ) <sub>4</sub> MoO <sub>4</sub>	dissolve CuMoO <sub>4</sub> in NH <sub>4</sub> OH	
Ag <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> MoO <sub>4</sub>	dissolve Ag <sub>2</sub> MoO <sub>4</sub> in NH <sub>4</sub> OH	
Zn(NH <sub>3</sub> ) <sub>2</sub> MoO <sub>4</sub>	dissolve ZnMoO <sub>4</sub> in NH <sub>4</sub> OH	

#### TABLE II — THIOMOLYBDATES

Al <sub>2</sub> (MoO <sub>3</sub> S) <sub>3</sub>	brown pp.	
Sb <sub>2</sub> (MoO <sub>3</sub> S) <sub>3</sub>	dirty green pp.	
BaMoO <sub>3</sub> S	brown pp.	sol. in HCl
Bi <sub>2</sub> (MoO <sub>3</sub> S) <sub>3</sub>	gray pp.	
CdMoO <sub>3</sub> S	pea green pp.	sol. in HCl
CaMoO <sub>3</sub> S	finely divided pp.	sol. in HCl
Cr <sub>2</sub> (MoO <sub>3</sub> S) <sub>3</sub>	brown pp.	sol. in HCl
CoMoO <sub>3</sub> S	brown pp.	sol. in HCl
CuMoO <sub>3</sub> S	red brown pp.	sol. in HCl and NH <sub>4</sub> OH
Fe <sub>2</sub> (MoO <sub>3</sub> S) <sub>3</sub>	light brown pp.	sol. in HCl, gives a char- trreuse colored sol.
FeMoO <sub>3</sub> S	brown pp.	sol. in HCl
PbMoO <sub>3</sub> S	muddy brown pp.	sol. in HNO <sub>3</sub>
MgMoO <sub>3</sub> S	caramel colored pp.	sol. in HCl
MnMoO <sub>3</sub> S	light brown pp.	sol. in HCl
Hg <sub>2</sub> MoO <sub>3</sub> S	brown pp.	
NiMoO <sub>3</sub> S	brown solution	sol. in H <sub>2</sub> O
Ag <sub>2</sub> MoO <sub>3</sub> S	brown pp.	sol. in NH <sub>4</sub> OH
Na <sub>2</sub> MoO <sub>3</sub> S	prepare by dissolving MoO <sub>3</sub> in sodium sulfide, brown solution results	sol. in HCl
SrMoO <sub>3</sub> S	light brown pp.	
ZnMoO <sub>3</sub> S	green brown pp.	
Na <sub>2</sub> MoOS <sub>3</sub>	add sodium hydroxide to MoS <sub>3</sub> , a light green solution results	

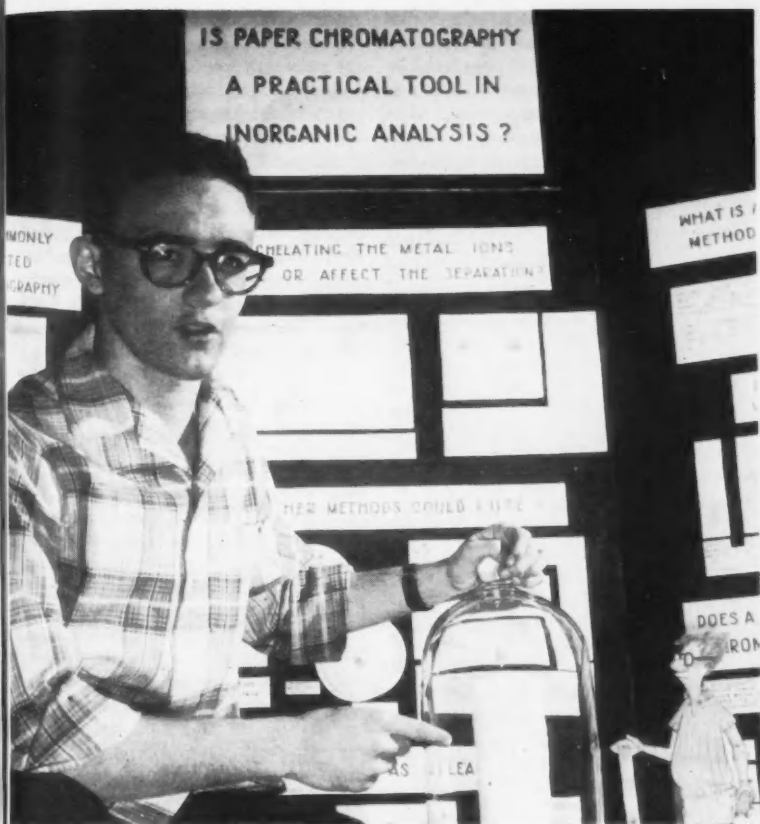
$\text{Al}_2(\text{MoS}_4)_3$	brown pp.
$\text{Sb}_2(\text{MoS}_4)_3$	cocoa brown pp.
$\text{PbMoS}_4$	brown pp.
$\text{HgMoS}_4$	brown pp.
$\text{NiMoS}_4$	brown pp.
$\text{Ag}_2\text{MoS}_4$	brown pp.
$\text{Na}_2\text{MoS}_4$	add sodium sulfide to $\text{MoS}_3$ , a cherry colored solution results

All of the preceding compounds were made by double decomposition unless stated otherwise.

TABLE III — OTHER COMPOUNDS

$\text{MoS}_3$	add $\text{H}_2\text{S}$ to acid solution of ammonium paramolybdate	metallic luster black brown pp.
$\text{MoS}_2$	heat $\text{MoS}_3$	brown
$\text{Mo}_2\text{S}_3$	add sodium sulfide to $\text{MoCl}_3$	brown pp.
$\text{MoSe}_3$	add $\text{H}_2\text{Se}$ to acid solution of ammonium paramolybdate	brown pp. quickly reduced to Mo blue
$\text{Mo}_2\text{O}_3$	reduce molybdate solution with zinc and $\text{HCl}$	black pp.
$\text{MoO}_2$	heat ammonium paramolybdate	black powder
$\text{Mo}_2\text{O}_5$	add sodium hydroxide to Mo blue	black pp.
$\text{MoO}_3 \cdot \text{H}_2\text{O}$	oxydized $\text{MoO}_2$ with $\text{H}_2\text{O}$	white creamy compound
$\text{MoCl}_3$	electrolyzed $\text{HCl}$ solution of ammonium paramolybdate	intense green solution light brown when dilute
$(\text{NH}_4)_2\text{MoCl}_5 \cdot \text{H}_2\text{O}$	saturate $\text{MoCl}_3$ solution with ammonium chloride	brick red pp.
$\text{CuMoCl}_5$	double decomposition with $(\text{NH}_4)_2\text{MoCl}_5$	light yellow pp.
$\text{HgMoCl}_5$	double decomposition	cream colored pp.
$\text{Na}_3\text{Mo}(\text{SCN})_6$	add $\text{NaSCN}$ to $(\text{NH}_4)_2\text{MoCl}_5$	deep red colored solution may be extracted with ether
$2\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 \cdot x\text{H}_2\text{O}$	acidify solution of sodium silicate and molybdate	yellow solution
$3(\text{NH}_4)_2\text{O} \cdot 5\text{MoO}_3 \cdot 2\text{MoO}_4?$	added $\text{H}_2\text{O}_2$ to ammonium paramolybdate	lemon yellow solution
$\text{K}_2\text{MoBr}_5$	saturate $\text{MoCl}_3$ solution with $\text{KBr}$	brown solution
$\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O} \cdot \text{MoO}_4$	add equivalent amount of oxalic acid to acid solution of ammonium paramolybdate	translucent crystals, parallelepipeds
$3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 24\text{MoO}_3 \cdot x\text{H}_2\text{O}$	add an ammonium salt to a molybdate and phosphate and nitric acid	canary yellow pp.

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► CHROMATOGRAMS OF IRON, copper, manganese and nickel were prepared by John Douglas Reichert as part of his entry in the 16th Science Talent Search. In his report he answered "Yes" to the question on the sign in the background.

## Chromatography in Inorganic Analysis

by JOHN DOUGLAS REICHERT  
Stephen F. Austin High School, Austin, Tex.

► LAST YEAR I became interested in a method of analysis which was widely used in the organic field. Library research indicated that paper chromato-

STRY

graphy had many applications in this field and relatively few in the area of inorganic analysis. I wondered if this were because the method was not applicable in the inorganic field or if it were merely because possibilities had not been investigated. I decided to investigate.

### Experimental

I selected four common metallic ions, Fe, Cu, Mn, and Ni, and made 2N solutions of the chlorides of these cations. A sheet of filter paper about 12 x 12 inches was impregnated at two inch intervals about one inch from one edge with drops of each of the chloride solutions and one spot with a mixture of all four chlorides. The paper was then rolled into a cylinder with the impregnated edge becoming the bottom circumference of the cylinder. This filter paper cylinder was then placed upright in a shallow dish containing a solvent. A bell jar was placed over the cylinder and dish to insure an atmosphere saturated with solvent vapor.

As the solvent traveled up the paper by capillary attraction, the charged spots were brought into solution. The ions traveled up the paper at different rates of speed which depended on processes of absorption and partition. This difference in rate of migration caused the ions to separate. After the solvent front had advanced about eight inches up the paper, the cylinder was removed from the solvent container, dried, and sprayed with reagents which formed colored compounds with the various ions. In this way the various components could be identified.

### Choice of Solvent

The solvent used is very critical

since the rate of migration varies with each solvent. In attempting to find the optimum solvent for these cations, I investigated all of the alcohols, many of the ketones, benzene, carbon tetrachloride, carbon disulfide, pyridine, and water, with various amounts of hydrochloric acid of different normalities. I found the percentage of acid to be a very critical factor. The solvents found to be best suited for my requirements were (a) 75% acetone with 25% 12N HCl (b) 75% methyl ethyl ketone with 25% 12N HCl (c) n-butanol saturated with 12N HCl (d) 87% acetone with 13% 4N HCl.

### Developers

To form colored compounds for identification, a great number of developers were investigated, such as dimethylglyoxime, sodium diethyldithiocarbazide, S-diphenylcarbazine, potassium ferrocyanide, benzidine, 8-quinolinol, fluorescein, hydrogen sulfide, ethylene diamine tetraacetic acid, sodium peroxide, ammonia vapor, and others. I found that the best method of developing these ions from the standpoint of ease, speed, and contrast was (a) exposing the chromatogram to ammonia vapor and air and then (b) spraying the chromatogram with dimethylglyoxime. This combination of developers produced an orange-brown confirmation for iron, bright blue for copper, dark brown for manganese, and a bright red for nickel.

Various other methods of chromatography were investigated, such as two dimensional, strip, streak, disc, descending development, and column techniques. The two dimensional techniques were used to attain still

greater separation of the spots. The strip chromatograms were extremely useful in testing the great number of solvents which I investigated. Various filter papers were investigated. Whatman's No. 1 was best for the cylindrical chromatograms. Whatman's No. 44 was found useful in the disc chromatograms. In an attempt to vary the  $R_F$  or % migration, ethylene diamine tetraacetic acid, dimethylglyoxime, and other chelating agents were investigated. The larger ring shaped ions offer a challenge which demands still further research on my part.

A method having been developed which was applicable in resolving mixtures which contained equal amounts of the four cations, I then made up solutions of (a) 70% iron with 10% copper, 10% manganese, and 10% nickel (b) 70% copper with 10% of each of the others (c) 70% manganese (d) 70% nickel (e) 90% iron with  $3\frac{1}{3}\%$  of each of the other cations. Using the method which I had developed, I was able to resolve all of the mixtures.

Since I could resolve mixtures which contained a great abundance of one of these elements, I decided to attempt to resolve an actual alloy. Monel and Inconel, which contain iron, copper, manganese, and nickel were separately dissolved in aqua regia and subjected to the chromatographic methods. These alloys were easily analyzed with my techniques.

#### Quantitative Chromatography

As this year began, I decided to continue the line of work which I had begun last year. Several opportunities for continuation presented themselves. One of the most obvious

of these areas was an attempt at quantitative estimation. Again I searched available literature in five libraries. Because of the colorimeters and other expensive equipment required, I was not as interested in the elution methods as I was with spot size and density considerations. I became familiar with the work of Fisher, Parsons, and Morrison, three gentlemen who together discovered that in many instances in the organic field the area of a spot is directly proportional to the logarithm of its quantity. It appeared to me that if this discovery could be made applicable to the inorganic field, it would be an excellent method for quantitative analysis of alloys.

Since in the analysis of an alloy, one is interested in a percentage composition instead of the actual amount of material contained on the paper, I made a certain basic modification in the technique as it had been used in the organic field. A "standard" mixture was made which contained equal amounts of 2M solutions of each of the four cations. This solution then contained an equal number of each of the ions. Then without tedious work with lambda pipettes or other measure of the quantity applied, this test solution was spotted on the paper. Other spots of known percentages, which were to serve as test "unknowns", were spotted on the same sheet. After the chromatogram was developed, each of the areas into which the "standard" solution had been separated, although unequal in area, could be assigned the same arbitrary quantity unit. A convenient unit, 1000, was selected for each of the "standard" solution's areas. Then I attempted to discover if the area

of one of the components was to the area of the corresponding component of the unknown as the logarithm of the "standard's" quantity (3,000) was to the logarithm of the "unknown's" quantity. The ratios for each component were solved and the antilogarithms found. These antilogs were summed and the summation divided into the separate antilogs. These quotients, when multiplied by 100, should, according to my hypothesis, give the percentage composition. About fifty chromatograms served to establish that my method was accurate to within 10%. The method was found to be applicable and successful in analyzing both alloys, Monel and Inconel.

I devised a unique method for measuring the areas of the spots. By using carbon paper or other tracing techniques, the perimeter of the spot was transferred to graph paper. The irregular figure was then converted into a polygon whose every vertex was on some intersection of the lines of the graph. By doing this I was able to utilize an interesting theorem of mathematics which I had discovered in *Mathematical Snapshots* by Steinhaus. The theorem states that if a polygon exists so that each of its vertices is some point on a lattice of whole numbers, the area of the polygon may be found according to the formula:  $A = P/2 + i - 1$ . "P" is the number of lattice points on the perimeter of the polygon and "i" is the number of lattice points on the inside of the polygon.

#### Electrography

Since I had been successful in developing a method for analyzing alloys and solutions containing iron,

copper, manganese, and nickel both qualitatively and quantitatively, I decided that a logical step would be to work out solvents and applications for resolving other constituents common to alloys. At this point a chemist informed me of a practical problem which, I thought, might be susceptible to solution by chromatography. It seems that if alloys plated with cadmium are welded, fumes are given off which are toxic to the welder. It seemed logical that the qualitative techniques of chromatography would have application here. In searching the literature for possible suggestions, I discovered another method of analysis which I thought might have application. The method was known as electrography. Electrographic analysis can be exemplified by connecting the anode from a series of four  $1\frac{1}{2}$  volt dry cells to the sample to be analyzed. The cathode of the series is connected in such a way that current must travel through a piece of filter paper soaked in an electrolyte solution such as potassium chloride. The electric potential causes atoms in the sample to become cationized and, in such soluble form, be deposited on the filter paper. After one or two minutes, the apparatus may be disconnected and specific spot tests applied to the paper for qualitative identification purposes.

This method displays all of the advantages of chromatography — (a) easy (b) cheap (c) quick (d) little experience required — with the added advantage that the unknown sample does not need to be dissolved in acid or otherwise marred.

It appeared that the method might be useful in determining rapidly and easily if cadmium were present in an



alloy. Electrograms of a cadmium plated object were run and I attempted to obtain a specific reagent for a spot test. Feigl's *Spot Tests* suggests S-diphenylcarbazine or ferrous dipyriddy iodide. I was not satisfied with either reagent since their intense color tends to mask the test under the conditions which I imposed. Remembering the utilization of  $(\text{NH}_4)_2\text{S}$  in high school qualitative analysis, I tried it as a test for cadmium. The test was successful, but, in the presence of a large amount of iron, the test was sometimes masked. For this reason and because in many instances a spot test might not be satisfactory for other cations, I investigated two possible avenues.

One idea was to use a chelating agent to keep interfering ions from masking a test. One of my next steps is to investigate still further this possibility. Preliminary work with the Versene chelates is encouraging.

The other idea was to "charge" a chromatogram electrographically. I worked out this technique myself and obtained successful results. I still need to find a better solvent for separating cadmium from iron, copper, manganese, and nickel, but a solvent of 45% butanol, 45% isopropyl alcohol, and 10% 5N HCl gives a resolution that allows cadmium to be easily identified. The combination of techniques was successful.

Realizing the advantages found in not destroying the sample which is to be analyzed, I used the combined pro-

cedures in separating the constituents of the alloys, Monel and Inconel.

I next wondered if the quantitative techniques were still valid when electrographic and chromatographic techniques were combined. Investigation revealed that, when a 2M "standard" solution was used and the charge to be analyzed was made under conditions of 6 volts for 1, 2, or 3 minutes, the area of the spot was not directly proportional to the logarithm of the quantity, but, instead, directly proportional to the quantity itself.

I was alarmed until a chemist pointed out that in electrolytic cells, the number of ions in solution is sometimes proportional to the quantity and sometimes to the logarithm of the quantity. This appears to be a close parallel.

To continue in this line, my next step is to vary the molarity of the "standard" solution from 0.1M to 10M, establish a concentration curve, and attempt to determine the point at which the logarithm becomes the important consideration instead of the quantity itself.

This project has been a great source of enjoyment to me. While working in this area I have established what appears to be a useful method of inorganic qualitative and quantitative resolution. I have also had success in illustrating a possible application for electrography and in developing a technique for combining two new methods of inorganic analysis.



Answers to CHEMISTRY QUIZ on page 42.

1, 1; 2, 3; 3, 3; 4, 4; 5, 3



## STS Awards Tripled

► THE NATION'S top 40 science-minded high school seniors, picked in the 17th Annual Science Talent Search, will share a total of \$34,250 in scholarships and awards. This is more than triple the amount awarded to previous winners of the annual nationwide search for promising research scientists.

The increase means that the grand scholarship to the top winner of the Search, which was formerly \$2,800, is now \$7,500. Four other science

scholarships now range from \$6,000 to \$3,000 and each of the other 35 finalists will receive a \$250 award. In addition, each of the 40 finalists receives a five-day all-expense-paid trip to Washington, D.C., to attend the Science Talent Institute in the spring.

The Science Talent Search is supported financially by the Westinghouse Educational Foundation and conducted by Science Clubs of America and administered through Science Service.

### ✓ Chemistry Quiz ✓

*Directions:* Mark within the parentheses corresponding to the answer you think is *most nearly correct*. Answers are on page 41.

1. An element found in all proteins but not in carbohydrates is
  - ( ) 1. nitrogen
  - ( ) 2. phosphorus
  - ( ) 3. sodium
  - ( ) 4. sulfur
2. The elements in the atomic table are arranged according to
  - ( ) 1. the numbers of electrons in their nuclei
  - ( ) 2. the numbers of electrons in their outer orbits
  - ( ) 3. their atomic numbers
  - ( ) 4. their atomic weights
3. Flint, the rock used by primitive man for making instruments, is primarily a compound of
  - ( ) 1. carbon
  - ( ) 2. iron
  - ( ) 3. silicon
  - ( ) 4. sulfur
4. Which of the following gives a different flame test from the others?
  - ( ) 1. borite
  - ( ) 2. chalcopyrite
  - ( ) 3. chalcocite
  - ( ) 4. halite
5. Which of the following is *not* an antibiotic?
  - ( ) 1. cycloserine
  - ( ) 2. eulucin
  - ( ) 3. oxytocin
  - ( ) 4. soframycin

These questions have been taken from Science Aptitude Examinations used in previous years as part of the annual Science Talent Search. Complete copies (with answers and norms) of many previous examinations are available at 10c each from Science Service, 1719 N St., N.W., Washington 6, D.C.

The Product That  
Couldn't Be Made

## Electromanganese

by WINSLOW W. BENNETT

*Metallurgical Sales Engineer, Foote Mineral Company*

► LIKE THE bumble bee, which violates aerodynamic theory but goes ahead and flies anyway, Electromanganese® by all yardsticks of experience was once considered a scientific impossibility. So, at least, concluded several metallurgical authorities in the early thirties, after rather extensive investigations of the electrolytic process.

From strictly theoretical considerations, manganese is too high in the electromotive series to be readily deposited from aqueous solution. In fact, the next metal above it — aluminum — must be deposited from a fused salt bath. Those skilled in the art of electrochemistry will point out that, in the deposition of manganese metal from solutions, the operating conditions must be very carefully controlled — otherwise hydrogen gas, and not metal, will be produced.

Despite this, and many more difficulties inherent in the production of manganese metal, there have also existed some very sound incentives for developing a workable process. Manganese is widely used as a valuable alloy for steel, aluminum and other metals. The higher quality alloys — such as the stainless steels — cannot tolerate more than trace amounts of carbon, phosphorus, and lead. Because they contain such impurities in excess of tolerable limits the more common forms of manganese, such as ferro-manganese and thermit man-

ganese, are restricted in their usefulness as alloying materials. A pure form of manganese is, therefore, a very valuable metallurgical tool.

In the early 1930's, Sheldon and his co-workers at the Bureau of Mines worked out a laboratory process for the electrodeposition of high purity manganese metal. If the process could be developed to commercial scale, and if a metal both high in purity and low in cost could be produced, it seemed likely that new frontiers in metallurgy might indeed be opened.

### A New Company

The Electro Manganese Corp. was formed in 1939 to develop the process on a commercial scale, but almost immediately ran into production difficulties. The transition from laboratory to commercial plant in an old Knoxville, Tenn., furniture plant was lengthy and arduous. After failure of the original plant, the process was rebuilt, from the ground up. Two years later reliable production was achieved at the rate of 72,000 pounds per month.

In March, 1956, the company became the Electromanganese Division of Foote Mineral Company and is now the world's leading electrolytic manganese producer, with two new plants and 15,000,000 pounds per year annual capacity. A \$2,000,000 expansion is underway.

Originally the purpose of developing a high purity electrolytic man-



► CHIPS OF *Electromanganese* after stripping from the cathode.

ganese was to compete with thermit manganese. The goal was realized early. After overcoming several manufacturing difficulties electrolytic manganese was priced competitively with thermit manganese.

#### **Manufacturing Procedures**

Figure 1 shows a simplified flow sheet for the manufacture of electrolytic manganese metal. Manganese ores, after blending, are ground and mixed with a carbonaceous material.

This mixture is fed to an electrical-

ly heated rotating tube furnace and the carbon in the mixture reacts with the manganese dioxide ( $MnO_2$ ) to form manganese oxide ( $MnO$ ). The green  $MnO$  is now soluble in sulphuric acid, and the insoluble residues are removed. Additional purification and filtration steps eliminate undesirable impurities such as iron, nickel, cobalt and molybdenum.

A prime requirement for electro-deposition of manganese from sulphate solutions is that the feed solution to the cells be extremely pure.

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The pregnant solution of manganese sulphate is fed to the cells, where the manganese is electrolytically deposited on stainless steel cathodes. When the laden cathodes are ready for stripping, they are flexed in rubber rolls. The manganese, being brittle as glass, readily parts company with the stainless sheet.

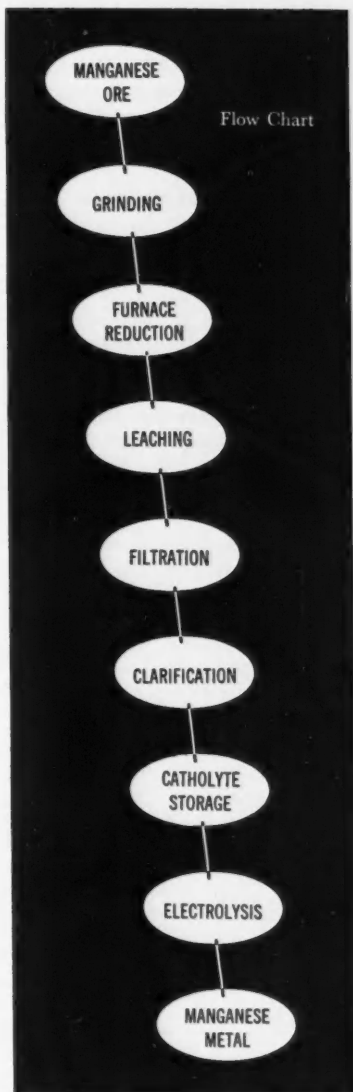
The electrolytic manganese from the stripping operation is ready for market as No. 1 metal. If lower hydrogen content is required the metal is treated in an annealing type furnace. This removes nearly all the objectionable gas.

Further treatment of Electromanganese in the presence of pure nitrogen gas at elevated temperature produces nitrided electrolytic manganese, a recently developed product called Nitrelmang®. A special continuous furnace, designed to maintain close control of both time and temperature, is used for this purpose. The product,  $Mn_4N$ , is the preferred nitride of manganese because of its stability at elevated temperatures. It has a theoretical limit close to 6.0 per cent  $N_2$  content. Two grades are produced in the Nitrelmang operation: one containing 5.5-6.0 per cent  $N_2$ , the other a partially nitrided product containing 4.5 per cent  $N_2$ .

#### End Uses

The steel industry accounts for the largest consumption of Electromanganese. Within this industry the market consists of important consuming areas.

**Stainless Steel:** There are some 30 distinct types of stainless steels, many of them with several variations. As every metallurgist knows, these alloys are grouped into metallurgical fami-



lies. Alloys containing primarily chromium and nickel with an iron base are austenitic. Those whose primary alloying element is chromium are ferritic or martensitic, depending on whether they are hardening or non-hardening.

#### Free Machining Steels

Producers of free-machining steel find that Nitrelmang Grade B, containing  $4\frac{1}{2}\%$   $N_2$ , can be used to advantage to make nitrogen additions to C-1212 and C-1213, the open hearth Bessemer-equivalent grades. Nitrelmang eliminates those problems associated with use of calcium cyanamid as a nitrogen source, since it does not introduce large quantities of combined carbon and calcium, which are undesirable for a low carbon steel (carbon 0.09% maximum).

#### Low-Carbon Open Hearth Steels

Considerable work has been done within the last two years on quality improvement of aluminum-killed deep drawing steels by addition of electrolytic manganese to the ladle in place of medium carbon ferro manganese. In some instances marked

quality improvement has been shown. These steels are low in carbon, 0.06% and under.

#### Non-Ferrous Applications

Use of electrolytic manganese in non-ferrous metallurgy has spread to numerous alloys of copper, aluminum, and zinc. Producers of brass, manganese-bronzes, and nickel-silver alloys were among the earlier users of this new metal, which by virtue of its purity at prices competitive with thermit manganese, managed to gain rapid and complete acceptance within this group. It is introduced to the brass mills either directly into the pots or via a master-alloy of 30% Mn-70% Cu made up by the smelting and refining companies.

The aluminum industry also consumes some Electromanganese in high-purity aluminum alloys.

#### Chemical Applications

Because of its high purity, Electro-manganese is used as a raw material for the preparation of pure chemical salts for the paint industry as well as other applications in pharmaceutical and catalytic work.

## On the Back Cover

► THE MAN on the ladder is examining some cabbages that have been treated with 100 micrograms of gibberellin once a week for two months. The cabbages on the floor did not undergo treatment. The scientist is Dr. S. H. Wittwer, Michigan State University, who is conducting research on growth promoters under a grant from Chas. Pfizer & Co., Inc. (See pages 3, 15, 19 and 28.)

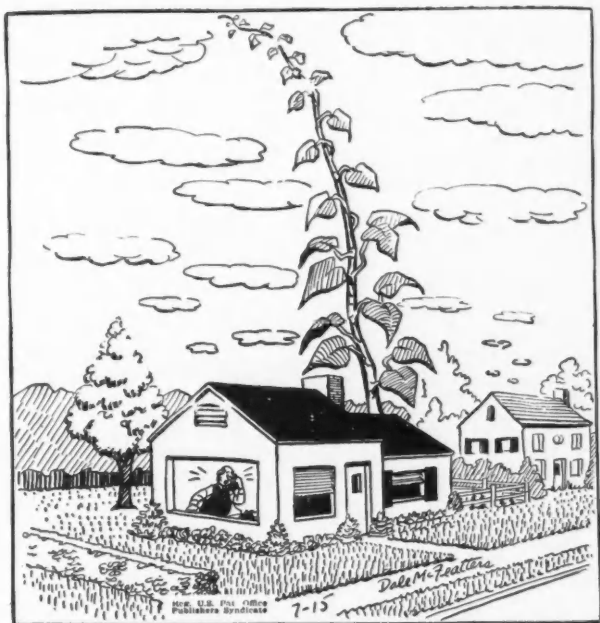
## See Cats Helping Diabetes Study

►CATS can serve humanity by helping doctors learn more about human diabetes, it appears from a report by Drs. J. Buse, K. Gundersen and F. D. W. Lukens of the University of Pennsylvania, Philadelphia, to the American Diabetes Association.

When cats are given a synthetic chemical related to anti-arthritis cortisone, they get diabetes, the Pennsylvania researchers found.

The cats develop ravenous appetites and fat bellies and their limbs get very thin. The diabetes is very mild and slow in developing. These features of the cat disease, the scientists point out, should make it especially useful for learning more about the kind of diabetes, with overeating and obesity, that develops in humans.

The synthetic chemical that produces the diabetes in the cats is 9-alpha-fluorohydrocortisone.



► "Jack's Garden Supplies? About those beans you sold me . . ."

## Book Condensations

EXPERIMENTING WITH CHEMISTRY — Burton L. Hawk — *Science Service*, 96 p., illus., \$2.00. A guide for the beginning chemical experimenter as well as a description of practical processes and explanation of reactions for advanced students. Complete range of home laboratory experiments plus special sections on blow pipe analysis, metallurgy, sympathetic inks, spontaneous combustion and spectacular reactions.

CHEMISTRY — Michell J. Sienko and Robert A. Plane — *McGraw-Hill*, 621 p., illus., \$6.75. Based on the lectures given in the large introductory chemistry course at Cornell University. Great emphasis is placed on the principles sometimes at the expense of descriptive details.

INTRODUCTION TO CHEMISTRY — Joseph C. Muhler, Charles S. Rohrer and Ernest E. Campaigne — *Prentice-Hall*, 452 p., illus., \$6.75. Giving biology students a chemical background by presenting an elementary treatment of physiological chemistry and both general and inorganic chemistry.

SCIENCE AND HUMAN LIFE — J. A. V. Butler — *Basic Books*, 163 p., \$3.95. A "personal attempt" to put recent scientific discoveries into perspective and to discuss their human implications. The author is a physical chemist.

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